CATALYTIC OXIDATIONS OF ORGANIC SUBSTRATES
BY TRANSITION METAL SALTS

By

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This work is dedicated to my grandmother, Sylvia Stickle--

She will always be with me.

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## KEY TO ABBREVIATIONS

MeCN = acetonitrile

oct = ethyl hexyl octanoate

hfacac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione

tfa = trifluoroacetate

Ph = $C_6H_5$

BPI = 1,3-bis(2'-pyridylimino)isoindoline

AIBN = azo-bis(isobutyronitrile)

t-BuOOH = tert-butylhydroperoxide

bpy = bipyridine

terpy = terpyridine

py = pyridine

biq = biquinoline

TMP = 5,10,15,20 tetramesityl porphyrin

TPP = 5,10,15,20 tetraphenyl porphyrin

TMC = 1,5,9,13 tetramethyl-1,5,9,13-tetraazacyclohexadecane

dmp = 2,9-dimethyl-1,10-phenanthroline

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Chairman:  Russell S. Drago
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The use of transition metal complexes for the catalytic oxidation
of organic substrates has been of interest to chemists for more then 100
years.  Their uses have ranged from initiating reactions to transferring
an atom to particular organic substrates.  Understanding the reactivity
and mechanisms of these reactions has both industrial and biological
implications.

The use of cobalt complexes for the autoxidation of alkanes is well
documented in the literature.  In most cases, the cobalt complex
functions as a peroxide decomposition catalyst.  We have demonstrated
that the cobalt-acetonitrile complex, $[Co(NCCH_3)_4](PF_6)_2$, functions both
as a radical initiator and as a peroxide decomposition catalyst under
mild reaction conditions.  This initiation characteristic makes this
reactivity novel.

The use of ruthenium complexes with nitrogen-based ligands has been reported in the literature to be capable of oxidizing a variety of organic substrates. These complexes mimic several naturally occurring enzymes, such as Cytochrome P-450. By modifying the ligands, dramatic changes in reactivity can be achieved. We report here the use of a sterically hindered ruthenium complex, $[Ru(dmp)_2(S)_2](PF_6)_2$ (dmp = 2,9-dimethyl-1,10-phenanthroline, $S = CH_3CN$, $H_2O$ or "O"), capable of oxidizing both olefins and alkanes selectively. The mechanisms of these reactions have been determined to proceed differently for each class of substrate.

This sterically hindered ruthenium complex demonstrated unique reactivity towards the hydroxylation of alkanes. The reactivity and mechanism of the oxidation of methane and other small alkanes were investigated. The ability for this catalyst to oxidize methane under mild reaction conditions shows promise in the conversion of this abundant feedstock to a storable fuel.

# CHAPTER 1

## GENERAL INTRODUCTION

The nature of catalytic processes has been a concern of chemists since chemistry became an experimental science.[1] In 1836 Berzelius[2] observed enhanced chemical activity, and, to focus attention on the phenomena, he gave it a name catalysis. Catalytic oxidations of organic compounds by molecular oxygen also have a long history.[3] This stems from Lavoisier's explanation of combustion, which marks the beginning of what we know today as modern chemistry. During the past century, the oxidation of petroleum hydrocarbon feedstocks by transition metal complexes has become an important part of the world's chemical industry. In 1977 over 5000 metric tons of organic chemicals were produced through oxidation processes in the United States alone.[4] These numbers have grown dramatically in recent years, making oxidation processes extremely important.[5] Transition metal catalyzed processes play a vital role in the control of the selectivity of the partial oxidation of alkanes, olefins, and aromatic hydrocarbons to useful products. If this is indeed the age of petroleum, with 90% of organic compounds derived from raw materials, it is also the age of catalysis.[6,7] The majority of petrochemical processes presently being used today are catalytic, with many important ones being catalytic oxidations.[8-10]

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Besides the industrial importance of oxidation processes, understanding many of these reactions have significant biological implications. Although enzymatic pathways are influenced to a large extent by the protein structure associated with the catalyst, the fundamental chemical steps resemble those occurring with simpler metal complexes. Understanding the mechanism and reactivity of many of these reactions can further our understanding of many enzymes and the oxidation processes which are carried out in living organisms. Many enzymes, in particular monooxygenases, are thought to contain metal-oxo moieties which are the active centers for these systems. Since enzymes are among the most efficient and selective catalysts known, understanding their reactivity can help develop and improve many industrial processes.

The majority of liquid phase transition metal catalyzed oxidations of organic substrates fall into three broad categories:

(1) Free radical autoxidation reactions, such as the Mid-Century/Amoco Process for the conversion of p-xylene to terephthalic acid, Equation 1-1;
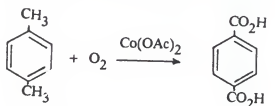


Equation 1-1

(2) reactions involving nucleophilic attack on coordinated substrates such as the Wacker Process for oxidizing ethylene to vinyl acetate, Equation 1-2;

$$CH_2=CH_2 \ + \ 1/2 \ O_2 \ + \ HOAc \ \xrightarrow[CuCl_2]{PdCl_2} \ CH_2=CHOAc \ + \ H_2O$$
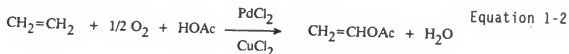
Equation 1-2

and (3) metal-catalyzed oxygen atom transfer reactions from coordinated hydroperoxides or metal-oxo species to organic substrates. An example of this third category is the reaction of propylene with alkylhydroperoxides to give propylene oxide in the presence of a molybdenum catalyst, Equation 1-3.

$$CH_3CH=CH_2 + ROOH \xrightarrow{\text{Mo compounds}} CH_3CH\text{-}CH_2 + ROH \qquad \text{Equation 1-3}$$
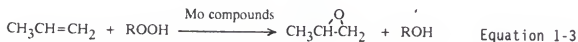
Of these, only the first, the autoxidation reaction represents the direct reaction of molecular oxygen with an organic substrate.[11]

The oxidation of hydrocarbons is a highly exothermic process, as indicated by the heats of combustion in Table 1-1. This exothermicity, approximately 105 kcal/mole for each mole of $O_2$ consumed, accounts for the use of hydrocarbons to power automobiles, airplanes and ships, as well as to generate much of our electricity. Carbon (coal) is somewhat less exothermic in its combustion, whereas CO and $H_2$ are somewhat more. In spite of the highly favorable thermodynamics for the oxidation of hydrocarbons, flammable materials can exist in our atmosphere due to the normally unfavorable kinetics of oxidation reactions at ambient temperatures.[12] These unfavorable kinetics have been a challenge to chemists for many years.

Table 1-1

Heats of Combustion for Hydrocarbons

| Substance | $-\Delta H$(kcal/mol)[a] | $nO_2$[b] | $\Delta H/n$ |
|-----------|--------------------------|-----------|--------------|
| Methane | 211 | 2 | 105 |
| Propane | 526 | 5 | 105 |
| Cyclohexane | 937 | 9 | 104 |
| Benzene | 782 | 7.5 | 104 |
| Carbon(charcoal) | 97 | 1 | 97 |
| CO | 68 | 0.5 | 136 |
| $H_2$ | 68 | 0.5 | 136 |

[a]For complete combustion to $CO_2$ and $H_2O$ (liq.) taken from *the Handbook of Chemistry and Physics*, 64th Ed., pp. 1878-1932. Chemical Rubber Publishing Co., Cleveland, 1983-84.
[b]The number of moles of $O_2$ required for complete combustion to $CO_2$ and $H_2O$.

# CHAPTER 2

## ALKANE OXIDATIONS BY
## COBALT(II) SALTS

### Introduction

Around the turn of the century, it was recognized that many oxidation reactions involved the formation of organic peroxides.[13] Criegee[14] made an important contribution in 1939 when he showed that the primary product of the autoxidation of cyclohexene is the allylic hydroperoxide. Subsequent mechanistic studies of the interaction of simple hydrocarbons and molecular oxygen carried out in the 1940s provided the basic concepts for the development of the free radical chain theory of autoxidation.[15-18] Although initial studies were concerned with the prevention of autoxidation reactions, it was soon realized that the controlled oxidation of hydrocarbons could be a useful method for synthesizing a wide range of oxygenated products. While autoxidation (referring to the oxidation with molecular oxygen) can be spontaneously initiated, it is commonly promoted by metal complexes, often in trace quantities. Studies on the effects of metal ions on the autoxidation process were studied during the early 1900s by Haber and Weiss, who formulated the classical mechanism for metal catalyzed decomposition of peroxides.[13,19] (Figure 2-1) In this reaction, once the alkyl radical is formed it readily reacts with $O_2$ to produce an alkylperoxide radical, which in turn forms the hydroperoxide. This

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hydroperoxide can then decompose in one of two pathways. It can dimerize to form a proposed tetra-oxo intermediate, which then decomposes to the alcohol, ketone and a mole of $O_2$. This intermediate has not been shown to exist experimentally. Alternatively, the alkylperoxide radical can react with the metal complex, which decomposes to the alcohol and ketone.

Sawyer and co-workers[20,21] have studied the mechanism for the decomposition of peroxides using an iron(II) complex. In this work, he showed that when a reducing agent, such as phenylhydrazine, was added to an alkylhydroperoxide in the presence of Fe(II), exclusively alcohol was observed as the decomposition product. This occurs because all of the iron remains as Fe(II), which is the source of the alkoxy radicals, and subsequently the alcohol in the proposed Haber-Weiss decomposition mechanism discussed above.

Mimoun and co-workers[22,23] have extensively studied the ability for transition metals to catalyze the decomposition of peroxides. In this work he has shown that the cobalt-peroxy complex, Co(BPI)(OAc)(OO-t-Bu), (BPI= 1,3-bis(2-pyridylimino)isoindecline) was an efficient peroxide decomposition catalyst. This work suggests that the formation of a cobalt(III)alkylperoxide intermediate plays an important role in the cobalt catalyzed peroxide decomposition pathway. This was the first work which gives experimental evidence for a metal-alkylperoxy intermediate. The nature of the chelating ligand was found to exert a profound influence on the existence and stability of the cobalt(III) alkylperoxide intermediate, and therefore on the rate of peroxide

$$In_2 \longrightarrow 2In\cdot$$

$$In\cdot + RH \longrightarrow R\cdot$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$$

$$RO_2H + M(II) \longrightarrow RO\cdot + M(III)OH$$

$$M(III)OH + RO_2H \longrightarrow M(II) + RO_2\cdot + H_2O$$

$$RO\cdot + H \longrightarrow ROH$$

$$2RO_2\cdot \longrightarrow [ROOOOR] \longrightarrow R=O + ROH + O_2$$

$$RO_2\cdot + M(II) \longrightarrow MOOR \longrightarrow M(III)OH + R=O$$

Figure 2-1 Classical Autoxidation and Peroxide Decomposition Pathway.

decomposition. Mimoun proposed that the formation of the cobalt(III) alkylperoxo complex results from the reaction of alkylperoxides and the cobalt(II) complex involving a one-electron oxidation of the metal. The decomposition of the cobalt(III)alkylperoxide complexes mainly leads to the formation of the initial cobalt(II) compound, with both ketone and alcohol being formed. The proposed mechanism for this reaction involves the homolytic cleavage of the O-O bond of the peroxide. This results in an alkoxy radical, which is the source of any alcohol observed in the reaction.

The rapid rate of the radical chain reaction is advantageous for producing oxygenated products. Utilizing this reactivity involves controlling the selectivity, an important aspect of any process. The control of selectivity is difficult to achieve due to formation of the highly reactive radicals formed. Once initiated, an autoxidation reaction is also difficult to control, often hard to stop short of $H_2O$ and $CO_2$. Although difficult to control, selective autoxidation processes do exist and some with only moderate selectivity are presently the basis for industrial processes.

## Background

The cobalt-catalyzed oxidation of hydrocarbons by molecular oxygen represents one of the largest scale applications of homogeneous catalysis.[4] These oxidations are the basis for several industrial processes. The synthesis of terephthalic acid from p-xylene (the Mid-Century/ Amoco Process)[24] is one such process. Typically, this oxidation is performed in acetic acid with a mixture of cobalt(II) and

manganese(II) acetates and bromides as the catalyst. Bromide is said to
be unique among the halides in its catalytic activity toward alkanes.[25]
The reason for this is bromide ions are known to be a radical initiator
for the autoxidation of alkanes.[26,27] The acetic acid is used to keep
any intermediates and by-products in solution. The desired product,
terephthalic acid, is very insoluble in acetic acid, as well as in other
organic solvents. This reaction is typically carried out under
stringent conditions of 195-205°C and 30 atmospheres pressure. In a
typical reaction a variety of other oxygenated products is also
observed. These products range from dicarboxylic acids to lactones.

Another industrially important oxidation process is the production
of acetic acid from the oxidation of butane. This reaction is achieved
using a soluble cobalt(II) salt under stringent conditions (Equation 2-
1)[4,11]

$$n\text{-}C_4H_{10} \longrightarrow CH_3\underset{O}{\overset{}{C}}C_2H_5 \longrightarrow CH_3COOH \qquad \text{Equation 2-1}$$

This reaction is carried out at 150-225°C and 800 psig $O_2$. Despite
these extremely rigorous conditions, this process has achieved a great
deal of popularity due to the abundance of butane as a feedstock.
However, the carbonylation of methanol by a rhodium carbonyl complex is
quickly taking over as the method of choice for the formation of acetic
acid.[22]

The production of adipic acid is another extremely important
oxidation process utilizing the autoxidation mechanism described above.
Adipic acid is used for a variety of different industries ranging from

an additive in food products to a precursor for Nylon 6,6. The
production of adipic acid has been carried out with subtle modifications
by the same process used in the early 1940s. The commercial process,
carried out by du Pont involves the oxidation of cyclohexane to a
mixture of products referred to as KA oil (a mixture of cyclohexanol and
cyclohexanone). The catalyst used in this reaction is a cobalt (II)
carboxylate salt. Again this oxidation reaction is carried out under
stringent conditions of 165°C and 10 atmospheres.[4,11,13] Once formed, the
KA oil is further oxidized in a second step to produce adipic acid. The
first step of the reaction proceeds with a 60-70 % selectivity to the
alcohol and ketone. Typically low conversions are maintained to prevent
the further oxidation of the alcohol and ketone to undesirable
products.[11,26,27] In this reaction a radical initiator, such as a bromide
salt, which is the source of bromine atoms, is necessary to initiate the
radical process. Once initiated, the reaction proceeds as outlined in
Figure 2-1. The cobalt(II) complex is used as a peroxide decomposition
catalyst.

Tolman and co-workers[12,28] from du Pont have extensively studied the
conversion of cyclohexylhydroperoxide to cyclohexanol and cyclohexanone.
Alternative catalysts for the decomposition of cyclohexylhydroperoxide
for use in the industrial process were investigated. One such cobalt
complex, Co(BPI), (BPI = 1,3-bis(2'-pyridylimino)isoindoline), was found
to have an increased lifetime, compared to the industrial catalyst
$Co(oct)_2$, (oct = ethyl hexyl octanoate). This complex was found to be a
less efficient peroxide decomposition catalyst than $Co(oct)_2$. This
Co(BPI) complex was also compared to several cobalt porphyrin systems,

which were found to have a limited lifetime due to the decomposition of
the porphyrin ring. Based on the cost efficiency of using Co(oct)$_2$ it
was determined that this catalyst would remain as the catalyst used in
the industrial process.

## Experimental

### Reagents and Equipment

All reagents were reagent grade or better. All silver salts were
purchased from Aldrich. Anhydrous cobalt(II) chloride was purchased
from Alfa. Both the benzene and the cyclohexane were spectral grade and
were purchased from Fischer Scientific. The cyclohexane was distilled
prior to use and stored over P$_2$O$_5$. The acetonitrile used throughout
this chapter was distilled over P$_2$O$_5$ and stored over 4A activated
molecular sieves.

Gas chromatography (GC) was carried out on a Varian 3300 instrument
utilizing packed, 8-ft, stainless steel columns and both flame induced
detector (FID). Analysis and calibration curves were obtained using 15%
DEGS (diethylene glycol succinate) support on Chrormosorb W (80/100
mesh) purchased from Altech. All products were compared to standards.
A Varian 4290 integrator automatically calculated peak area and
retention times. The GC-MS was performed using a Varian 3400 gas
chromatograph interfaced with a Finnegan MAT ITDS 700 Mass Spectrometer.
The column employed was a 15 m dbl capillary column. All IR spectra
were recorded either as Nujol mulls or KBr pellets on a Nicolet 5DXB
spectrometer and were background corrected. A Perkin-Elmer Lambda 6
Ultraviolet (UV)-visible spectrometer was used to collect UV-vis

spectra, all spectra were background corrected. The NMR spectra were recorded on a multinuclear Varian VXR 300 MHz spectrometer or on a General Electric QE 300 MHz spectrometer. The electrochemical studies were carried out with a PAR model 175 Universal Programmer attached to a model 173 potentiostat/galvanostat. The electrodes incorporated were a platinum working and auxiliary electrode, with a Ag/AgCl reference electrode used. All redox potentials were corrected to a standard hydrogen electrode for comparison purposes. Elemental analyses were performed on a service basis by the microanalytical laboratory at the University of Florida.

## Synthesis

Tetrakistrifluoroacetate cobalt(II) bis tetraphenylphosphonate, $[Co(tfa)_4](P(C_6H_5)_4)_2$, (tfa = $CF_3CO_2^-$) was prepared as described by Cotton.[29] In a 500 mL round bottom flask, stoichiometric quantities of $(C_6H_5)_4PCl$, $AgO_2CCF_3$ and anhydrous $CoCl_2$ were mixed together in 50 mL acetonitrile. The solution was stirred at room temperature for 15 minutes with the precipitation of AgCl. This blue solution was then filtered using a fine frit, and diethylether was added dropwise until the solution became cloudy. The solution was then covered and was allowed to stand for 8 hours. The resulting blue/violet crystals were filtered and washed with diethylether and dried under vacuum. The characterization of this complex is discussed in a later section. Calculated for $[Co(tfa)_4](P(C_6H_5)_4)_2$: %C = 56.52, %H = 3.36, %N = 0.00; Found %C = 56.71, %H = 3.34, %N = 0.00.

Bis-trifluoroacetato cobalt(II), Co(tfa)$_2$, (tfa = CF$_3$CO$_2^-$) was prepared using a modification of the literature procedure procedure.[30] In a 250 mL round bottom flask, stoichiometric quantities of AgO$_2$CCF$_3$ and anhydrous CoCl$_2$ were mixed together in 50 mL acetonitrile. This solution was allowed to stir at room temperature for 30 minutes, with the precipitation of AgCl. The pink/red solution was filtered and diethylether was added until the solution became cloudy. The solution was allowed to stand for 5 hours. The resulting pink crystals were filtered and were washed with diethylether, and dried under vacuum. The characterization of this complex is discussed in a later section. Calculated for Co(tfa)$_2$: %C = 9.20, %H = 0.00, %N = 0.00; Found %C = 9.32, %H = 0.21, %N = 0.00.

Tetrakisacetonitrile cobalt(II) bis-hexafluorophosphate, [Co(NCCH$_3$)$_4$](PF$_6$)$_2$ was prepared "in situ" as follows: In a 200 mL round bottom flask, stoichiometric amounts of anhydrous CoCl$_2$ and AgPF$_6$ were combined in acetonitrile. The solution was stirred for 15 minutes with the precipitation of AgCl. The AgCl was filtered. The resulting blue solution was tested for Ag$^+$ and Cl$^-$, using standard trace element tests. These elements in trace amounts will inhibit the activity if this complex. The characterization of this complex is discussed in a later section.

Bis(aquo)bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)cobalt(II), Co(hfaca)$_2$(OH$_2$)$_2$ was prepared as reported in the literature.[31] To 1.2 grams of CoCl$_2$ dissolved in 25 mL of dimethylformamide, 2.08 grams of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacac) was added. A solution of 0.75 grams of sodium acetate in 30 mL of distilled H$_2$O was added.

The solution was stirred for 2 hours and poured into a 250 mL beaker of crushed ice. After stirring for an additional 5 minutes, the solid was filtered using a medium frit. This solid was washed with water and vacuum dried at room temperature overnight. This orange solid was then dissolved in 25 mL of acetonitrile and recrystallized with the addition of water. The resulting yellow solid was washed with ethanol and vacuumed dried. Calculated for $Co(hfaca)_2(OH_2)_2$: %C = 23.30, %H = 2.33, %N = 0.00; Found %C = 23.37, %H = 1.69, %N = 0.04.

## Scope of Catalysis

Apparatus. All pressurized oxidations were carried out in a modified Parr hydrogenation setup (Figure 2-2). This apparatus setup has previously been described by Zuzich and Davis.[32,33] This apparatus was equipped with a stainless steel pressurehead, constructed from Swagelok fittings and equipped with gas inlet and outlet valves, a standard pressure gauge, and a two-way ball valve, through which samples could periodically be taken during the course of a reaction. This apparatus was connected directly to a gas source though the gas inlet valve. The gas outlet valve was connected to tygon tubing, in order to direct the exit of the gas, and gas vapors into the back of the hood. The reaction vessel, a 250 mL Parr hydrogenation bottle, was attached to the pressurehead by a #6 silicone gum rubber stopper. A metal sheath was surrounding the bottle to minimize the amount of glass shards that would be produced in the event of an explosion. Sampling the reaction was performed in the following manner. A 1 mL gastight syringe, equipped with a Luerlok syringe valve and a 12-inch 16 gauge needle, was
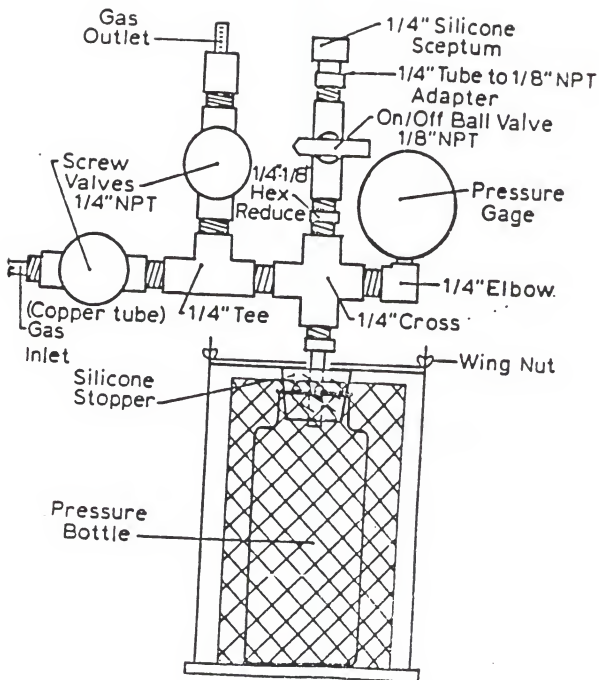
Figure 2-2    Standard Oxidation Pressure Apparatus
with Stainless Steel Pressurehead.

inserted though the septum at the top of the pressure head with the valve in the closed position. The needle was carefully guided through the ball valveinto the reaction mixture. The syringe valve was slowly opened, and a small aliquot withdrawn ( 0.3 mL). The valve was then closed and the needle withdrawn. The sample was placed into a 1 dram screw top vial until analysis is performed. With practice, this procedure can be carried out safely and quickly, with no apparent lose of pressure. The sample is analyzed via GC, GCMS, GCIR and NMR. Samples analyzed by GC were injected three times to obtain an error for each sample.

Oxidation procedure. Typical reactions involved 30 mL of substrate ( 100 fold excess to catalyst), 1 mL of an internal standard (benzene), and $10^{-5}$ moles of catalyst. The reactions were carried out at 75°C silicone oil bath, monitored by an Omega 6100 temperature controller and thermocouple under initial pressures of 40 psig $O_2$. Air was used inplace of $O_2$ as a safety factor when working with volatile substrates. The reaction mixtures were stirred using a magnetic stir bar, controlled by a magnetic stirrer beneath the oil bath. The oil bath was circulated by an overhead stirrer. The oxidation reaction was terminated after 12 hours to assure that all catalysis which was occurring was a result of the cobalt complexes and not an autoxidation process. In a typical uncatalyzed reaction, trace amounts of products were formed after 20 hours of reaction time.

Safety precautions. The combination of molecular oxygen and hot organics are potentially very explosive. Extreme caution should be taken when during the setup and dismantling of the oxidation reactions,

to avoid any sparks which can cause a violent explosion. General precautions should be followed such as (1) pressurize and vent <u>only</u> cool solutions; (2) direct outlet gases away from any source of sparks; and (3) be aware of the explosive limits of the solvent, substrate, and the oxidant before preceding with an oxidation reactions.

    <u>Calculations</u>. Gas chromatography was used in all cases to quantify the amount of products being produced. Calibration curves relating moles of products to the relative peak areas were used for all products quantified. A standard procedure involved the preparation of standard solutions containing varying, known concentration of product, and a constant quantity of standard in the solvent used. Five consecutive GC injections of each concentration gave a statistically valid value for the area percent of the product peak. The mole ratio can be determined from the moles of products and moles of standard. This ratio was then plotted against the ratio of the area percents of the product and standard. The area percentages were obtained from the integration of the peak areas of the GC chromatogram by the integrator. From the graph of the mole ratio to area percent ratio, the number of moles of products could be obtained.

## Results and Discussion

    The initial catalyst used in these studies was the tetrakistrifluoroactetato cobalt(II) complex, $[Co(tfa)_4](P(C_6H_5)_4)_2$ which was synthesized as described in the experimental section. Due to the limited solubility of this complex in cyclohexane, an alternative

solvent was necessary to dissolve the metal complex. This catalyst is highly soluble in acetonitrile; therefore the oxidation of cyclohexane by this cobalt(II) complex was initially carried out in a biphasic solution consisting of cyclohexane and acetonitrile. Under our reaction conditions, 75°C and 3 atmospheres of pressure, these two liquids only have a limited solubility. After 12 hours of reaction time, cyclohexane was oxidized primarily to a 2:1 ratio of cyclohexanol to cyclohexanone yielding 13 turnovers (turnover = mole of product/ mole of catalyst). This reaction was terminated after 12 hours to assure all catalysis occurring is a result of the cobalt complex and not an autoxidation process. Unless otherwise stated all reactions in this chapter were run for 12 hours. A typical GC trace of this reaction solution is illustrated in Figure 2-3. Under these reaction conditions the catalyst used by du Pont in the industrial process for the oxidation of cyclohexane $Co(oct)_2$, (oct= ethyl hexyl octanoate) is unreactive.

The primary products in the oxidation are cyclohexanol and cyclohexanone. In the industrial oxidation of cyclohexane, the solvent system used is KA oil. This solvent helps solubilize the industrial catalyst $Co(oct)_2$, (oct= ethyl hexyl octanoate) in the reaction mixture. To mimic this solvent system, cyclopentanone was added to our reaction mixture. Cyclopentanone was selected since it would not interfere in the analysis of the reaction products. Upon addition of this ketone to the biphasic mixture of acetonitrile/cyclohexane, the solution visually appeared to be one phase. Furthermore, as seen in Figure 2-4, carrying out the oxidation with the addition of cyclopentanone resulted in a large increase in activity (120 turnovers/12 hours). This reaction

A = Cyclohexane
B = Benzene
C = Acetonitrile
D = Cyclopentanone
E = Cyclohexanone
F = Cyclohexanol

TIME
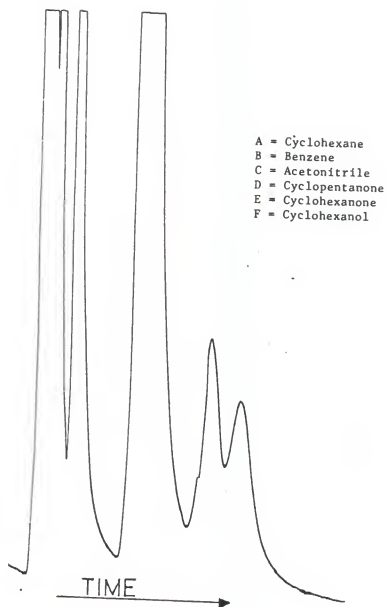
Figure 2-3    Standard GC Trace for the Oxidation of Cyclohexane.
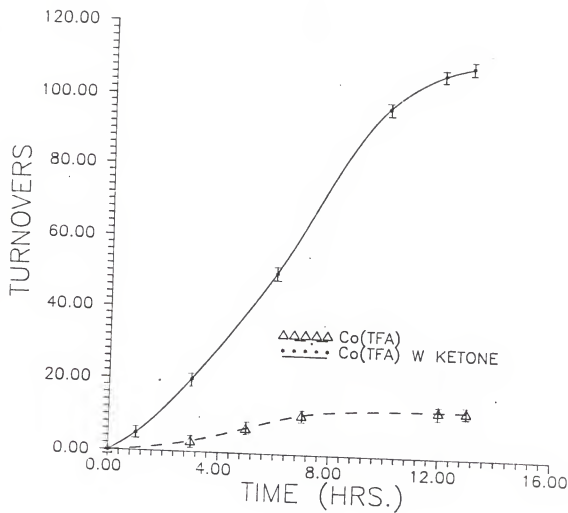
Figure 2-4   Oxidation of Cyclohexane by $[Co(tfa)_4](P(C_6H_5)_4)_2$ with and without added ketone at $75°C$ and 3 atmospheres.

proceeds with a 50 % selectivity to the alcohol and ketone. A variety of other products, such as carboxylic acids and lactones, is also observed. These products which are observed in a typical oxidation of cyclohexane are commonly observed in autoxidation reactions.[34] The nature of these ring opening products suggests an important role for the b-cleavage of cyclohexyloxy radicals generated during the reaction.[12] Early in the oxidation, when cyclohexanol and cyclohexanone are still minor, the major cyclohexyloxy radical will be the unsubstituted $CyO\cdot$; later the 1-hydroxycyclohexyloxy radical, formed via radical attack on A and K at their weakest C-H bonds, becomes an important sources of ring opening products (see Figure 2-5).[12]

The use of bis-trifluoroacetato-cobalt(II), $Co(tfa)_2$, for the oxidation of cyclohexane demonstrated comparable activity to that of $[Co(tfa)_4](P(Ph)_4)_2$. This is illustrated in Figure 2-6. The preparation of this complex was discussed in the preceding section. The activity of this two-coordinate cobalt complex is slightly greater then that of the four coordinate $Co(tfa)_4^{2+}$. This can be explained by the vacant coordination sites and less steric hindrance around the metal centers on this complex.

To determine the nature of the active species, a solution of anhydrous cobalt chloride in acetonitrile was used as a catalyst in the oxidation reaction. In this reaction the same product distribution, 60% alcohol : 40% ketone which was observed for the tetrakistriflouroacetate complex, was observed. This oxidation proceeded with less conversion than that seen with $Co(tfa)_4^{2+}$ (see Figure 2-6). In this reaction, the initially blue solution slowly turns pink as the reaction progresses.
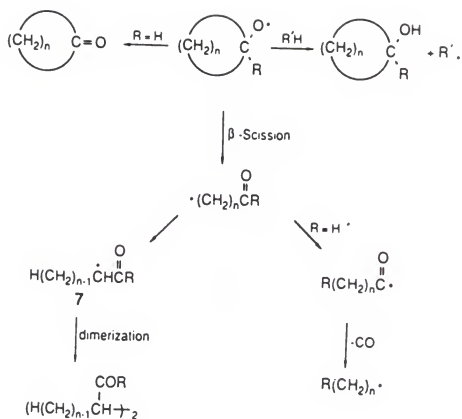
Figure 2-5    Proposed Formation of Ring Open Products during the
              Oxidation of Cyclohexane
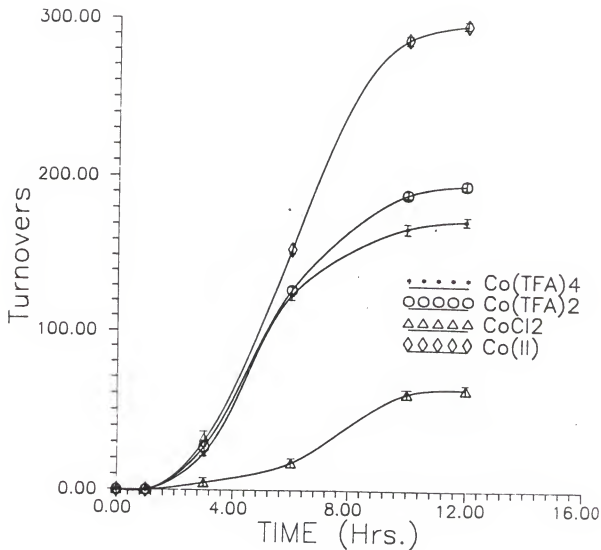
Figure 2-6    Comparison of Cobalt Catalysts for the Oxidation
of Cyclohexane at 75°C and 3 Atmosphere.

This pink color is characteristic of a octahedral hydrated cobalt(II) species. Based on these results the question arises if the active species is a tetrachlorocobaltate species.

The removal of the chloride ions from the $CoCl_2$ using $AgPF_6$, a weakly coordinating anion, would result in a cobalt species which could be viewed as a "naked metal ion," or a weakly solvated complex. The preparation of this complex in acetonitrile was described in the preceding experimental section. Since this complex was prepared "in situ" in acetonitrile, a biphasic system was formed upon mixing with cyclohexane. In a typical oxidation reaction, 29 Turnovers/12 hours resulted. Once again, to mimic the industrial system, the ketone, cyclopentanone was added to the reaction mixture. This formed a one phase system as previously seen with the $[Co(tfa)_4](PPh_4)_4$ system. This reaction mixture resulted in a large increase in activity (see Figure 2-6). In this reaction, 295 Turnovers/12 hours resulted. This reaction proceeded with a 53% selectivity, with 60% cyclohexanol and 40% cyclohexanone. Again, as observed with the $Co(tfa)_4^{2+}$ complex, the other products were a variety of ring opening products. Several characteristics of this reaction using this cobalt-acetonitrile species will be discussed below.

## Catalyst Characterization

Due to the weakly coordinating nature of $PF_6^-$, this counter anion is easily displaced by the solvent, acetonitrile used in the preparation of this complex, forming a solvated Co(II) ion paired species. The species being formed has a general formula, $[Co(NCCH_3)_x](PF_6)_2$. As seen

in Figure 2-7, a series of $^{19}F$ NMR experiments indicate that the $PF_6^-$ is not in the inner coordination sphere of the metal center. Starting with 0.5 M solution of $[Co(NCCH_3)_x[PF_6]_2$ in acetonitrile, several $^{19}F$ NMR spectra were obtained at various concentrations. The spectrum at 0.5 M showed a doublet due to the $PF_6^-$ (-69.8,-72.3 ppm). This doublet corresponds to that observed for $Na^+PF_6^-$ in acetonitrile. Diluting the solution with acetonitrile to 0.1 M and then $10^{-3}$ M led to no observable shift in the $PF_6^-$ resonance. Furthermore, the $^{19}F$ NMR spectrum of the catalyst solution containing a standard reaction concentration of cyclohexane and cyclopentanone, also shows no observable shift in the $PF_6^-$ resonance. Since coordination of $PF_6^-$ to a paramagnetic cobalt(II) would lead to a large isotropic shift, these experiments strongly suggest that the catalyst in solution is a solvated cobalt(II) with the general formula $[Co(NCCH_3)_x](PF_6)_2$ with dissociated $PF_6^-$ counter ion.

UV\Visible spectra of this complex at various concentrations were obtained to determine the geometry of the complex. A 0.01 M solution of the complex has a molar absorbtivity of 495, characteristic of a tetrahedral geometry (see Figure 2-8). Upon further dilution of the complex with acetonitrile to $10^{-3}$ M and $10^{-4}$ M the molar absorbtivity decreased to 470 and 452 respectively. Based on the NMR results and these molar absorbtivities, the predominant cobalt species in solution is the four coordinate complex, $[Co(NCCH_3)_4](PF_6)_2$ complex.

Catalyst Optimization

To determine the effect the solvent has on the reaction, the volume of acetonitrile used in the reaction was varied. These experiments are

Figure 2-7   $^{19}F$ NMR of $[Co(NCCH_3)_x](PF_6)_2$.
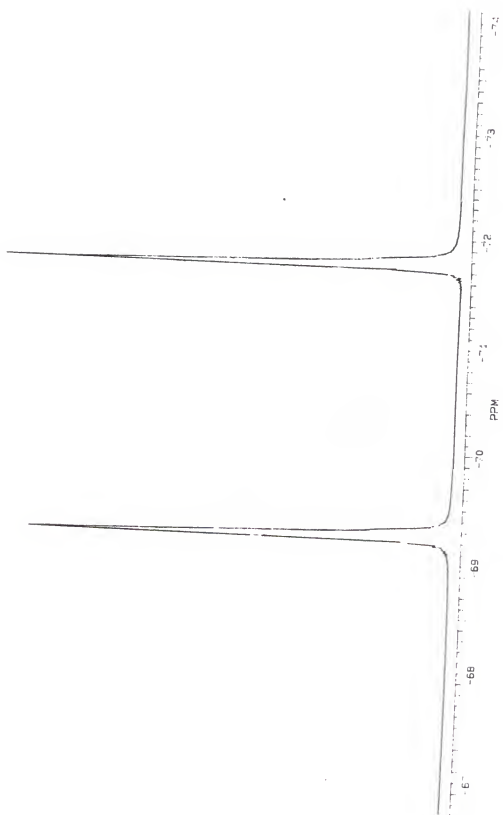
Figure 2-8    UV/Visible Spectrum of $[Co(NCCH_3)_4](PF_6)_2$ in Acetonitrile.
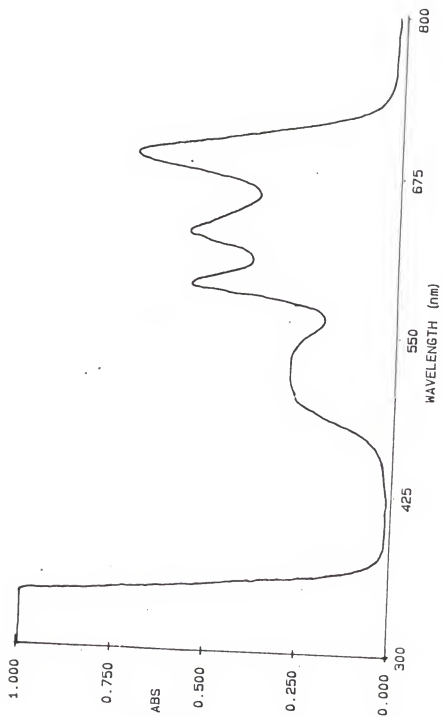
illustrated in Figure 2-9. The results show that as the concentration of acetonitrile was decreased, while holding the amount of cobalt constant and maintaining a total volume of 50 mL, there was an increase in the moles of products formed during 12 hours of reaction time. When the volume of acetonitrile is decreased below 2 mL, a loss in activity was observed. This loss is due to the insolubility of the catalyst solution in the cyclohexane/cyclopentanone solution. The results of these experiments indicate that this system, which visually appears to be one phase, is not a truly homogeneous solution. In a homogeneous system the volume of acetonitrile should have a minor dielectric effect on the overall activity, since the cobalt concentration in the total solution was constant in all cases. In a suspension, increasing the acetonitrile concentration would decrease the cobalt concentration on the surface of the droplet formed. We attribute the observed decrease in activity in our system to this phenomena.

The use of solvents other than acetonitrile was also investigated. No activity was observed using propionitrile, tetrahydrofuran (THF) or propylene carbonate. The larger size of these ligands, relative to that of acetonitrile, would make it more difficult for an oxidized cobalt complex to initiate an outer sphere electron transfer reaction from cyclohexane to cobalt. Acetone results in the same product distribution, although there is a 10-fold decrease in the number moles of products/12 hours as compared to acetonitrile. As seen in Figure 2-10, the formation of products cease after 12 hours of reaction time. After approximately 10 hours, the initial blue catalyst solution turns
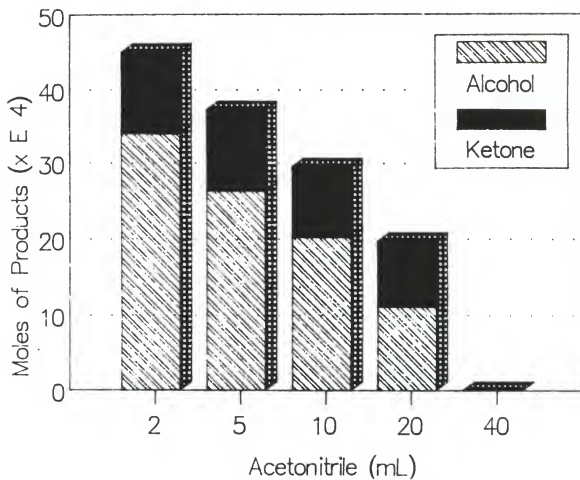
Figure 2-9    Variation in Acetonitrile for the Oxidation
             of Cyclohexane by [Co(NCCH₃)₄](PF₆)₂ at 75°C and 3
             Atmospheres.
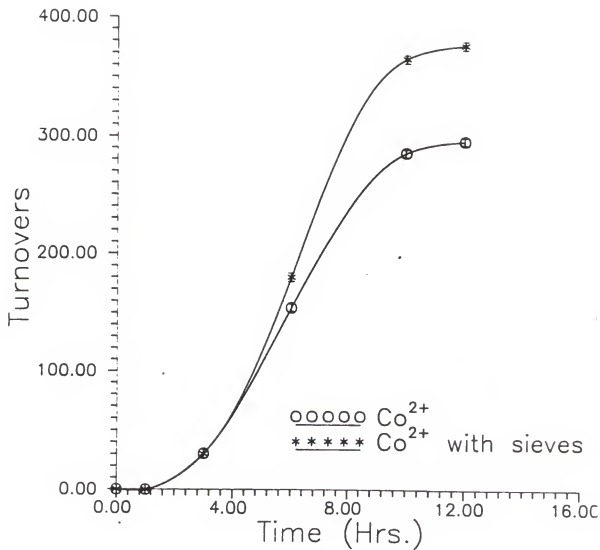
Figure 2-10   Addition of Sieves to the Oxidation of
              Cyclohexane by [Co(NCCH$_3$)$_4$](PF$_6$)$_2$ at 75°C and 3
              Atmospheres.

pink, characteristic of a octahedral cobalt complex. To determine if water, formed during the oxidation, is coordinating to the cobalt (II) and inhibiting this reaction, the following experiments were carried out. After 6 hours of reaction time, a small aliquot of water was added to the reaction mixture. Upon addition, the initially blue catalyst solution turned pink at once and the formation of oxidation products ceased. When 4A activated molecular sieves were added to the reaction mixture, prior to reaction, an increase in the number of moles of products was observed (Figure 2-9). Although the activated sieves can absorb 60% of their weight in water, the reaction stopped when only 25% of their weight in water was formed. Hydrogen bonding of the water to acetonitrile is a competing process, thus apparently increasing the water concentration in the acetonitrile to the point where it hydrates the cobalt (II) when approximately 25% of the total sieve capacity by weight is attained. The inhibition of the reaction by the water formed from the decomposition of peroxide is also reported with other cobalt complexes.[35,36] These experimental results indicate the formation of water inhibits the reaction. The use of acetonitrile dried over sieves, as well as the use of dried cyclohexane, shows a further increase in the products formed.

To determine if the use of a more strongly coordinating ligand system could prevent the loss of activity due to the formation of water, $Co(hfacac)_2$, (hfacac = 1,1,1,5,5,5 hexafluoro-2,4-pentanedione) was used as a catalyst for the oxidation of cyclohexane. In this reaction, a large induction period of 18 hours was observed. As the reaction progressed, a product ratio of 60% alcohol : 40% ketone was observed.

After 96 hours of reaction time the catalyst eventually died, although a lower conversion compared to the acetonitrile complex was observed. In 96 hours, 200 turnovers resulted. Although this complex had a much longer lifetime than $Co(NCCH_3)_4^{2+}$, the decrease in activity, compared to the cobalt-acetonitrile complex made this catalyst undesirable for further studies.

To further optimize the cobalt-acetonitrile system, the catalyst concentration was varied (Figure 2-11). Although doubling the catalyst concentration to $2 \times 10^{-5}$ moles resulted in an increase, a doubling in number of moles of products was not observed. Using this concentration of catalyst, $3.6 \times 10^{-3}$ moles of alcohol and ketone were obtained. Increasing the catalyst concentration to $4 \times 10^{-5}$ moles resulted in 4.7 $\times 10^{-3}$ moles of products being formed. When the catalyst concentration was decreased to $5 \times 10^{-6}$ moles the products formed decrease by 80 % from that of $10^{-5}$ moles of catalyst yielding $6.3 \times 10^{-4}$ moles of product. From these experiments, $10^{-5}$ moles of catalyst seems to be the optimum catalyst concentration for these reaction conditions.

Our next concern was in evaluating the selectivity of our catalyst. The total quantity oxygenated products formed were determined by capillary GC using standard silation techniques.[37] Using $10^{-5}$ moles of our catalyst, results in a 50% selectivity towards cyclohexanol and cyclohexanone and proceeds with a 5% conversion of the cyclohexane to total products. In the industrial process carried out by du Pont, a 3-5% conversion with 60-70% selectivity is obtained. The conversion of this reaction is kept low to prevent the further oxidation of the alcohol and ketone to undesirable ring-opened products. A large range
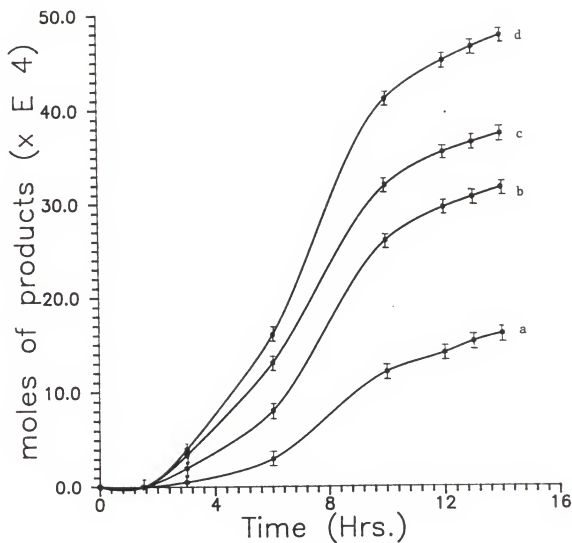
Figure 2-11    Variation of Catalyst Concentration for the
Oxidation of Cyclohexane  -  a) $10^{-6}$ moles
b) $10^{-5}$ moles c) $2 \times 10^{-5}$ moles d) $4 \times 10^{-5}$ moles.

of other products, are commonly observed in the oxidation of cyclohexane.[12] These products range from dicarboxylic acids to lactones. Decreasing the reaction time from 12 hours to 8 hours, using $[Co(NCCH_3)_4])(PF_6)$, results in an increase in selectivity to 75% with a decrease to 4% conversion. This increase in selectivity results from less of the alcohol and ketone

being further oxidized. Once formed, both of these products, cyclohexanol and cyclohexanone, are more easily oxidized than cyclohexane. By decreasing the catalyst concentration to $10^{-6}$ moles, a 91% selectivity to the alcohol and ketone is observed, but a large decrease to 1% was observed.

This oxidation using $[Co(NCCH_3)_4](PF_6)_2$ was next carried out under the more stringent conditions used industrially (165°C and 10 atmospheres) to determine the effect on the selectivity and conversion. Running the reaction using $10^{-6}$ moles of catalyst resulted in a substantial decrease in selectivity from 91% to 38%, although an increase in the total conversion to 5% was observed. Thus, under these more stringent conditions, $10^{-6}$ moles of our catalyst gives conversions comparable to $10^{-5}$ moles of catalyst at 75°C. This increased activity of our catalyst suggests that even lower concentrations of catalyst would be optimal at high temperature and pressure.

Mechanistic Studies

Various experiments were carried out on this catalyst system to investigate the mechanism of the reaction. As illustrated in Figure 2-12, various free radical experiments were performed. The addition of a
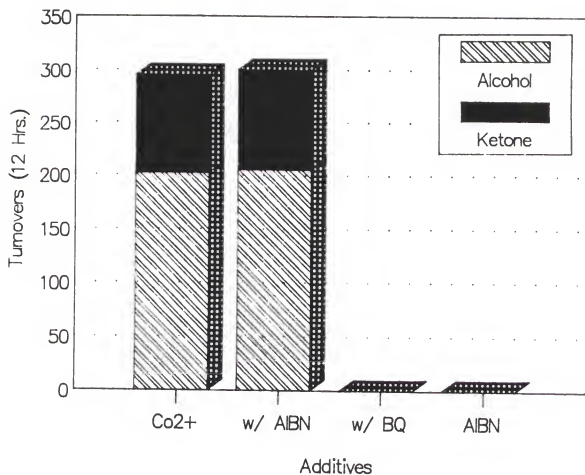
Figure 2-12    Free Radical Experiments for the Oxidation
of Cyclohexane at 75°C and 3 Atmospheres.

free radical inhibitor, benzoquinone, to the reaction results in no observed products. Adding AIBN (a free radical initiator, azo-bis(isobutyronitrile)) to the acetonitrile solution containing the cobalt complex had no effect on the reaction, and attempting to initiate the reaction with AIBN alone yielded no products in 12 hours of reaction time. These experiments indicate a free radical chain mechanism.

The oxidation of adamantane using this cobalt-acetonitrile species was also studied. Adamantane, a tetrahedrally symmetrical hydrocarbon, possessing four tertiary and twelve secondary carbon-hydrogen bonds was selected for study. The $C^2/C^3$ ratio (where $C^2$ is the total number of the oxidized products at the secondary position, and $C^3$ is the total amount of the tertiary alcohol formed) is commonly used as a probe in measuring the selectivity of a reaction being studied. From probability considerations alone, a totally nonselective reaction a $C^2/C^3$ ratio of 3. Hydrogen atom abstraction reactions using substituted ferric porphyrin systems, resulted in $C^2/C^3$ ratios of 0.2.[38,39] Reported nonradical reactions, such as Bartons "Gif" systems[40] which utilizes an iron catalyst have also been probed using this substrate. A $C^2/C^3$ ratio of 3.7 was reported. Modification of the "Gif" system has resulted in $C^2/C^3$ ratios as high as 15.[41] Based on these studies, it has been proposed that these "Gif" systems are proceeding via a non-radical mechanism. In a typical oxidation reaction using the cobalt-acetonitrile species at 75°C and 40 psig of pressure, adamantane was oxidized to 1-adamantanol (65%), 2-adamantanol (25%) and 2-adamantanone (10%). This corresponds to a $C^2/C^3$ = 0.53 indicative of a radical process.

The proposed mechanism for the oxidation of cyclohexane is illustrated in Figure 2-13. During the oxidation, a 2-hour induction period is observed. The nature of this induction period was investigated to determine whether the reaction is being initiated at low peroxide thresholds or if an oxidized cobalt species reacts with the substrate to initiate the reaction. At the beginning of the reaction $10^{-5}$ moles of t-butylhydroperoxide was added to determine if peroxides were initiating the reaction. Upon addition of $2 \times 10^{-5}$ moles of peroxide, no change in the induction period was observed. Another possible explanation of this induction period involves the oxidation of some of the cobalt(II) by $O_2$. To determine if this was the cause of the induction period, the catalyst in acetonitrile, in the absence of the substrate, was pressurized at 75°C for 2 hours, the length of the induction period. After this time, the substrate was added. The induction period for the oxidation reaction was found to decrease to approximately 1/2 hour as illustrated in Figure 2-14. This suggests that the oxidation of the cobalt ion is occurring during the induction period to produce a species that can react with the substrate forming a cyclohexyl radical. A variety of reactions involving metals such as $Co^{3+}$ or $Fe^{3+}$ have been reported to generate radical species via electron transfer processes.[11,42,43]

Electrochemical experiments demonstrated the feasibility of radical initiation via an electron transfer process. As seen in Figure 2-15 the cyclicvoltammogrm of the cobalt species in acetonitrile resulted in a quasi-reversible wave at a potential of 1.92 V vs. NHE. This potential is much higher than many cobalt complexes. This oxidation wave is

$$Co(CH_3CN)_4^{2+} \longrightarrow Co[OX]$$

$$Co[OX] + C_6H_{12} \longrightarrow C_6H_{11}\cdot + H^+ + Co(CH_3CN)_4^{2+}$$

$$C_6H_{11}\cdot + O_2 \longrightarrow C_6H_{11}O_2\cdot$$

$$C_6H_{11}O_2\cdot + C_6H_{12} \longrightarrow C_6H_{11}O_2H + C_6H_{11}\cdot$$

$$C_6H_{11}O_2H + Co^{2+} \longrightarrow C_6H_{11}O\cdot + Co(III)OH$$

$$Co(III)OH + C_6H_{11}O_2H \longrightarrow Co(III)O_2H_{11}C_6 + H_2O$$

$$Co^{2+} + C_6H_{11}O_2\cdot \qquad Co(III)OH + C_6H_{10}O \qquad Co(III)O\cdot + C_6H_{11}O\cdot$$

$$C_6H_{11}O\cdot + H \longrightarrow C_6H_{11}OH$$
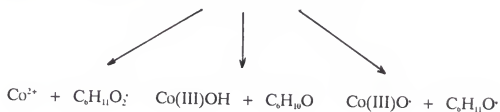
Figure 2-13    Proposed Mechanism for the Oxidation of Cyclohexane
by [Co(NCCH$_3$)$_4$](PF$_6$)$_2$.
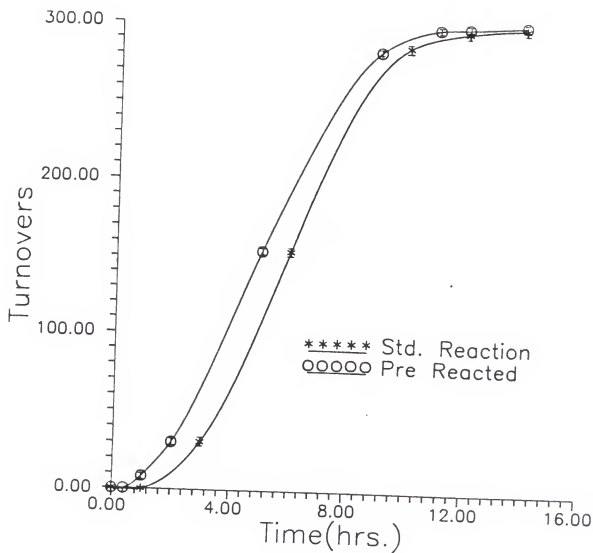
Figure 2-14    Pre-reaction of $[Co(NCCH_3)_4](PF_6)_2$ with 3 Atmospheres $O_2$ and 75°C for 2 Hours.

2.50

VOLTS vs. NHE

0.00
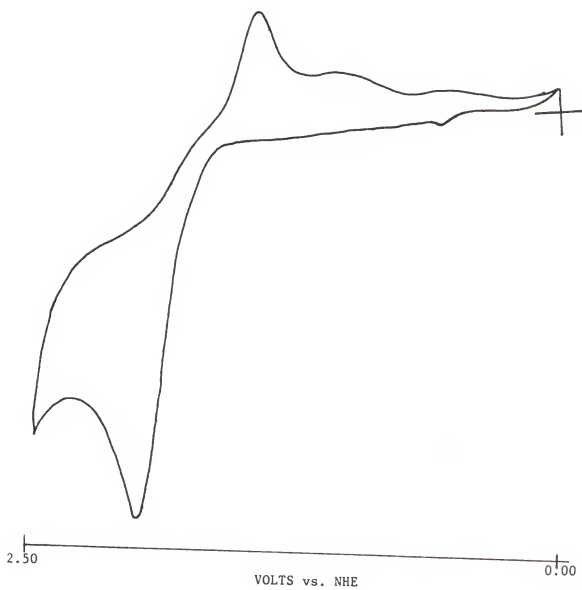
Figure 2-15    Cyclic Voltammetry of $[Co(NCCH_3)_4](PF_6)_2$
in Acetonitrile.

a result of the oxidation of $Co^{2+}$ to $Co^{3+}$. This potential is greater than that of cyclohexane which has an oxidation potential of 1.62 V vs. NHE. The electrochemistry of the commercial catalyst, $Co(oct)_2$, which showed no activity under our reaction conditions, resulted in an irreversible wave at 1.23V vs. NHE. This potential indicates that this oxidized cobalt species would be less efficient at initiating the reaction and explains the lack of activity of this catalyst under mild reaction conditions. Under the reaction conditions, a solution of anhydrous $CoCl_2$ in acetonitrile showed 1/3 the activity of the $[Co(NCCH_3)_4](PF_6)_2$. Cyclic voltammetry of $CoCl_2$ in acetonitrile resulted in an oxidation wave at 1.60V vs. NHE. This potential is comparable to that of cyclohexane in this system. The loss of activity which occurred with the formation of water, as previously discussed, has been supported by electrochemical studies. The addition of water to a solution containing the cobalt ion species in acetonitrile resulted in a decrease in the oxidation potential for the cobalt from 1.92 V to a value of 1.21 V vs NHE. This cobalt species is not a potent enough oxidant to remove an electron from cyclohexane, resulting in a loss of activity. Similar changes in the redox couple for Fe(II)/Fe(III) in acetonitrile have also been observed.[22]

During the 2-hour induction period, the buildup of the oxidized cobalt occurs until its concentration is high enough to initiate the reaction by reacting with cyclohexane to generate the cyclohexyl radical. The alkyl radical generated in the first step reacts readily with dioxygen forming the alkyl hydroperoxy radical. This radical then reacts with cyclohexane generating another alkyl radical and cyclohexyl

hydroperoxide. Once formed, the hydroperoxide then undergoes a Haber-Weiss decomposition mechanism[44] forming the observed products, cyclohexanol and cyclohexanone. The homolytic cleavage of the O-O bond of the peroxide, as proposed by Mimoun,[23] may be a source of the alcohol observed in the reaction.

To further understand the selectivity to the alcohol and ketone, the decomposition of peroxides by the cobalt complex must be understood. As shown in Figure 2.13, once formed, the alkylhydroperoxide is decomposed by either cobalt(II) or cobalt(III). If cobalt(II) decomposes the alkylperoxide, the product formed is the alcohol. On the other hand, if the alkylhydroperoxide is decomposed by the cobalt(III), the product formed is the ketone. In a standard reaction, if a reducing agent, such as phenylhydrazine is added to the reaction mixture, no ketone should be observed. When this reaction was carried out, we found an increase in the induction period from 2 hours to 10 hours. After the reaction was initiated, the major product observed was cyclohexanol. This increase in the induction period is due to the reducing agent preventing the formation of the cobalt(III) species, which is believed to initiate the reaction. This result is analogous to that observed by Sawyer[20], although Sawyer does not discuss an induction period in his reaction.

The effectiveness of the cobalt-acetonitrile species in catalyzing the decomposition of peroxides was studied using t-BuOOH as a model peroxide under the oxidation reaction conditions. The concentration of peroxide was measured using an iodometric titration procedure.[45] As illustrated in Figure 2-16, the cobalt-acetonitrile species decomposes

t-BuOOH more efficiently than that reported for the efficient CoBPI complex.[23,43] On the other hand, the commercial catalyst, $Co(oct)_2$ decomposes t-BuOOH as efficiently as our catalyst, $Co(NCCH_3)_4^{2+}$. With all of these catalysts, the formation of water causes inhibition and eventually the loss of the ability to decompose peroxides efficiently. This has been observed for other cobalt catalysts.[35,36] Furthermore, as illustrated in Figure 2-17, as the concentration of catalyst is increased, the quantity of peroxide decomposed also increases. This result is what would be expected for metal-catalyzed decomposition of peroxides as described in the preceding section.

Since the formation of water, resulting from the decomposition of peroxides, causes a loss of ability to decompose the peroxide efficiently, an alternative method for the formation of adipic acid is warranted. The feasibility of a co-catalyst system, which would selectively cleave the ring of cyclohexane, after the initial oxidation to the alcohol, resulting in a one step process for the formation of adipic acid should be further investigated. Such a system could eliminate many of the undesirable products which are commonly observed in this oxidation process.
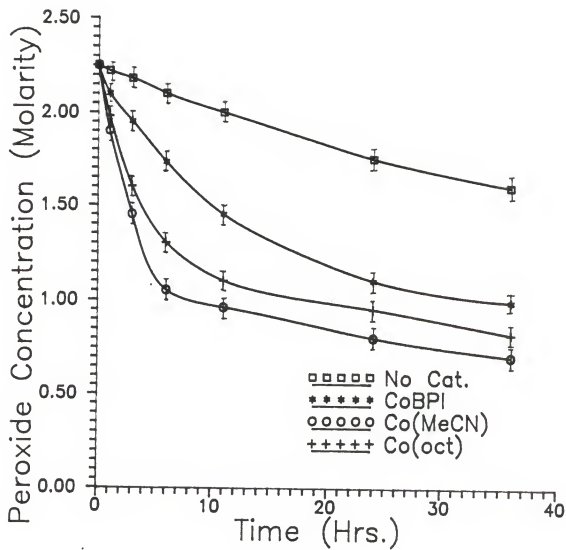
Figure 2-16   Decomposition of t-Butylhydroperoxide at 75°C and 3
Atmospheres.
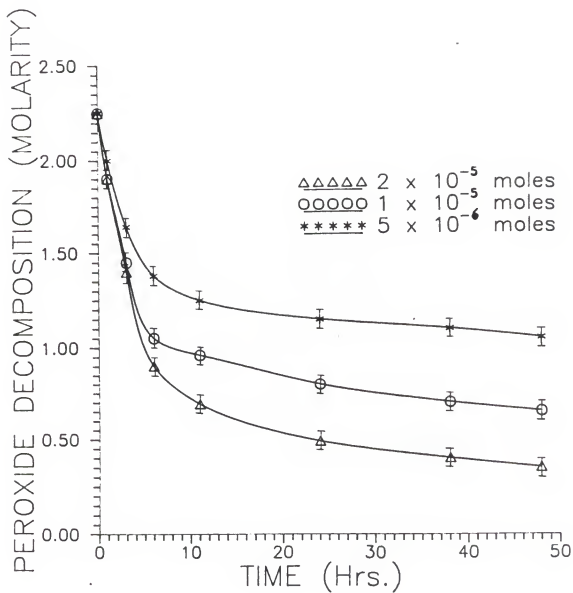
Figure 2-17  Variation in [Co(NCCH$_3$)$_4$](PF$_6$)$_2$ for the Decomposition of t-Butylhydroperoxide at 75°C and 3 Atmospheres.

CHAPTER 3

## SYNTHESIS AND CHARACTERIZATION OF
## RUTHENIUM DIMETHYLPHENANTHROLINE
## COMPLEXES

### Introduction

High valent metal-oxo complexes have attracted considerable
attention in recent years because of the potential use of these
complexes as catalysts for the oxidation of a variety of organic
substrates.[46] Many of these systems mimic a variety of enzymes, such as
peroxidases[47], as well as intermediates in oxygen atom transfer
reactions of cytochrome P-450[48,49] and the dioxygen reduction of
cytochromes oxidase.[50] An understanding of the redox chemistry mediated
by these enzymes has been hampered by the instability of these oxidized
iron-heme intermediates and by the lack of simple chemical models for
these reactive states.[51] Synthetic examples of an
oxoiron(IV)porphyrin[52,53] and an oxoiron(V) radical cation[54,55] are
known; however, the thermal instability of each of these complexes has
prevented the isolation of pure solids. The periodic relationship of
iron and ruthenium suggests that the latter may provide stable examples
of high valent metal-oxo complexes.

Groves and co-workers[56] have shown that a ruthenium porphyrin
system, Ru(TMP), (TMP = 5,10,15,20-tetramesitylporphyrin) can react
readily with $O_2$ to form a high valent $trans$-Ru(VI)(O)$_2$. This is one of

48

a very few examples of a ruthenium complex with a nitrogen based ligand system reacting directly with $O_2$ to form high valent ruthenium-oxo complexes. Kochi has shown[57] that the cis-Ru(VI)(O)$_2$Cl$_4^{-2}$ complex could be formed using iodosobenzene as an oxygen source. He proposed that this dioxo species could be formed from the direct oxidative addition of $O_2$ to the ruthenate anion but did not confirm this prediction experimentally. Furthermore, Collman[58] has reported that a ruthenium "picnic basket" porphyrin can reversibly bind $O_2$ leading to the formation of a Ru(IV)O species. The formation of this complex is proposed result from the cleavage of a 1-peroxo dimer.

Previous work in our laboratory[59] has shown that the sterically hindered, high valent cis-[Ru(VI)(O)$_2$(dmp)$_2$](PF$_6$)$_2$, (dmp = 2,9 dimethyl-1,10 phenanthroline) is a catalyst, or catalyst precursor for the aerobic epoxidation of olefins. This complex was found to be unstable at room temperature and difficult to isolate as a solid. Many nitrogen-based ruthenium complexes appearing in the literature[60,61] indicate that the favorable geometry of high valent dioxo complexes of ruthenium is the trans configuration. This is based on the fact that the trans isomer is more stable due to the lower energy of the HOMO($d_{xy}$).[62] INDO/1 semi-empirical molecular orbital calculations,[63] indicate the trans-dioxo complex is approximately 35 kcal mol$^{-1}$ more stable than the cis isomer. Due to this instability, the isolation of a cis-Ru(O)$_2$ species was unsuccessful. Based on these theoretical and experimental conclusions, we attempted to synthesize the precursors for this high valent ruthenium complex for potential use as an oxidation catalyst, as discussed in later chapters.

## Experimental

### Reagents and Equipment

All reagents were reagent grade or better. All silver salts were purchased from Aldrich. Both ruthenium trichloride and neocuproine were purchased from Aldrich. The cerium perchlorate solution was purchased from G.F. Smith. Ethylene glycol was purchased from Fischer Scientific and was used as received. The acetonitrile used in this chapter and the following chapters was distilled over $P_2O_5$ and was stored over 4A activated molecular sieves. The apparatus and equipment used in this section is described in the preceding chapter.

### Synthesis

*cis*-Ruthenium(II) bis(2,9 dimethyl-1,10 phenanthroline) dichloride monohydrate, $[Ru(dmp)_2Cl_2]\cdot H_2O$, was prepared with some modifications as described by Collin and Sauvage[64]. In a 500 mL round bottom flask, equipped with a reflux condenser and a thermometer, 1.0 grams (3.8 mmol) of $RuCl_3\cdot XH_2O$ was combined with 1.7 grams (8 mmol) of neocuproine monohydrate (dmp), and 2.5 grams (59 mmol) of LiCl in 25 mL of ethylene glycol. This solution was refluxed at 150°C under a nitrogen atmosphere for 6 hours. It is important not to allow the temperature to exceed 150°C during this time. Elevated temperatures lead to impure final products. After 6 hours, the heat was removed and 50 mL of acetone was slowly added to the dark purple solution while it is still hot. The solution is then allowed to cool to room temperature while continuously stirring. At this time 15 mL of distilled $H_2O$ is added to the reaction mixture. The solution was then filtered using a medium frit and the

purple microcrystalline solid was washed 3 times with 15 mL of distilled $H_2O$. The resultant solid was vacuumed dried at $50°C$ overnight. The characterization of this complex is discussed in a later section. Calculated for $[Ru(dmp)_2Cl_2] \cdot H_2O$: %C = 55.45, %H = 4.29, %N = 9.24; Found %C = 55.42, %H = 4.28, %N = 9.22.

*cis*-Ruthenium(II) bis(2,9 dimethyl-1,10 phenanthroline)-bisacetonitrile-bis(hexaflourophosphate), $[Ru(dmp)_2(NCCH_3)_2](PF_6)_2$, was prepared according to the following procedure. In a 100 mL round bottom flask, 0.1 grams of $Ru(dmp)_2Cl_2 \cdot H_2O$ was dissolved in 20 mL of acetonitrile. This solution needed heating to dissolve all of the $Ru(dmp)_2Cl_2 \cdot H_2O$. To this red solution, 1 drop of 1 M $HPF_6$ was added. This solution immediately turn yellow. To the solution 0.86 grams of $AgPF_6$ dissolved in a minimum amount of acetonitrile was added. The AgCl which precipitated out upon addition of $AgPF_6$ was filtered using a fine frit. To the resulting yellow solution, 15 mL of a saturated aqueous $NaPF_6$ solution was added. The resulting yellow/orange solid was filtered and washed with distilled $H_2O$. This solid was then dissolved in acetonitrile and recrystallized with diethylether. Single crystals of the bis-acetonitrile complex were obtained via diffusion techniques using diethylether. The characterization of this complex is discussed in a later section. Calculated for $[Ru(dmp)_2(NCCH_3)_2](PF_6)_2$: %C = 43.19, %H = 3.37, %N = 9.45; Found %C = 43.20, %H = 3.33, %N = 9.44.

*cis*-Ruthenium(II)bis(2,9 dimethyl-1,10 phenanthroline) diaquo-bis(hexaflourophosphate), $[Ru(dmp)_2(OH_2)_2](PF_6)_2$, was prepared using the following procedure. In a 100 mL round bottom flask, 0.1 grams of $Ru(dmp)_2Cl_2 \cdot H_2O$ was dissolved in 20 mL of distilled $H_2O$. The solution

had to be heated to completely dissolve all of the Ru(dmp)$_2$Cl$_2$·H$_2$O. This solution was then heated to 60°C for 30 minutes under a N$_2$ atmosphere. To the resulting red solution 15 mL of a saturated aqueous NaPF$_6$ solution in 0.1 M HPF$_6$ was added. This resulted in a brown precipitate. This solution was then stirred at 5°C for 2 hours. This additional stirring is necessary to displace any additional Cl$^-$ coordinated to the ruthenium center. At this time the dark brown precipitate was filtered and washed with 0.1M HPF$_6$ solution. The resulting solid was dried at room temperature under vacuum overnight. The characterization of this complex is discussed in a later section. Calculated for [Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$: %C = 39.85, %H = 3.32, %N = 6.64; Found %C = 39.69, %H = 3.26, %N = 6.61.

*cis*-Ruthenium(IV)oxo-bis(2,9 dimethyl-1,10 phenanthroline)(bis-hexafluorophosphate, [Ru(IV)(O)(dmp)$_2$(OH$_2$)](PF$_6$)$_2$, was prepared using the following procedure. In a 100 mL round bottom flask, 0.05g of [Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$ was dissolved in 20 mL of distilled water. The solution was gently heated to completely dissolve the diaquo complex. To the dark red solution 3 equivalents of a 30% H$_2$O$_2$ solution was added dropwise while the solution was stirred. The solution turned from dark red to orange/yellow upon addition of the H$_2$O$_2$. To this solution, 15 mL of a saturated aqueous solution of NaPF$_6$ was added until a precipitate formed. The yellow solid was filtered using a fine frit and washed 3 times with diethylether. The resulting solid was dried overnight under vacuum. Due to the difficulty of isolating the final product, this complex was often generated "in situ" and used for various studies. A variety of other oxidants can also be used in place of H$_2$O$_2$. These

include t-butylhydroperoxide, sodium hypochlorite and cerium(IV)perchlorate solution. In the cases when a hydroperoxide is not used, only 2 equivalents of oxidant are necessary. The characterization of this complex is discussed in a later section. Calculated for $[Ru(O)(dmp)_2(OH_2)](PF_6)_2$: %C = 39.95, %H = 3.09, %N = 6.66; Found %C = 39.80, %H = 2.99, %N = 6.52.

$cis$-Ruthenium(VI)dioxo bis(2,9 dimethyl-1,10 phenanthroline) bis(hexafluorophosphate), $[Ru(VI)(O)_2(dmp)_2](PF_6)_2$, was prepared "in situ" by the following procedure. In a 100 mL round bottom flask, 0.05g of $[Ru(dmp)_2(OH_2)_2]PF_6)_2$ was dissolved in 25 mL distilled water. Gentle heating was require to completely dissolve the diaquo complex. To this dark red solution, 7 equivalents of $H_2O_2$ were added dropwise while the solution was stirred. The red solution turned yellow upon addition of the 7 equivalents of $H_2O_2$. The characterization of this complex is discussed in a later section. Once again, other oxidants as described above, can be used in place of $H_2O_2$. For the cases in which a hydroperoxide is not used, only 4 equivalents of oxidant are necessary to generate the $cis$-Ru(VI)(O)$_2$ species.

## Characterization

Several spectroscopic methods were employed to identify and characterize the complexes synthesized in this chapter. These spectroscopic methods have been previously described in Chapter 2. In addition to the spectroscopic techniques discussed below, elemental analysis was used to give additional evidence for the formation of the

desired complex. The elemental analyse for each of the synthesized complexes are listed in the experimental section.

UV /Visible absorption data were collected and are listed in Table 3-1. It is well established that the intense low-energy absorption bands observed in Ru(II)(bpy)$_2$X$_2$ (bpy = bipyridine, X = halogen[65-67]) are assigned to metal-to-ligand charge transfer (MLCT) transitions of the type d$p$ (Ru) --- $p^*$(bipy). By analogy, the high extinction coefficients measured for the visible bands of dmp complexes in Table 3.1 strongly support the MLCT nature of the corresponding transitions. For each complex, the energy of the MLCT transition is exceedingly dependent on the nature of the ancillary ligands coordinated at the cis position. This can be seen in Figure 3.1, which illustrates a comparison of Ru(dmp)$_2$Cl$_2$·H$_2$O, [Ru(dmp)$_2$(NCCH$_3$)$_2$](PF$_6$)$_2$ and [Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$. In all 3 of these cases the ancillary ligands are in a cis configuration.

A variety of NMR experiments were performed to further characterize the ruthenium(II) dmp complexes. A typical $^1$H NMR of the bis acetonitrile complex, cis-[Ru(dmp)$_2$(NCCH$_3$)$_2$](PF$_6$)$_2$ is illustrated in Figure 3-2. In this spectrum, the two methyl groups on the phenanthroline ligands result in two non-equivalent resonances at 1.71 ppm and 3.29 ppm. The two non-equivalent methyl groups support the formation of a cis complex. In the aromatic region of this spectrum, from 7 to 9 ppm, there are well resolved resonances due to the protons on the phenanthroline rings. This region shows 3 different AB patterns (3,4;5,6;7,8) characteristic of a dissymmetric substituted

Table 3-1

Electronic Properties of $Ru(dmp)_2X_2$ Complexes.

| Compound | UV/VIS Bands $\lambda$ max, nm ($10^{-3}$ $\epsilon$, mol$^{-1}$ L cm$^{-1}$) | |
|---|---|---|
| $Ru(dmp)_2Cl_2 \cdot H_2O$ | 584 (6.89) | 492 (5.42) |
| $Ru(dmp)_2(OH_2)_2{}^{2+}$ | 496 (6.87) | 412 (4.95) |
| $Ru(dmp)_2(NCCH_3)_2{}^{2+}$ | 440 (6.87) | 372 (6.52) |

Figure 3-1

UV/Visible Spectra of -
a) $cis$-[Ru(dmp)$_2$Cl$_2$]·H$_2$O in CH$_2$Cl$_2$.
b) $cis$-[Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$ in H$_2$O.
c) $cis$-[Ru(dmp)$_2$(NCCH$_3$)$_2$](PF$_6$)$_2$ in CH$_3$CN.
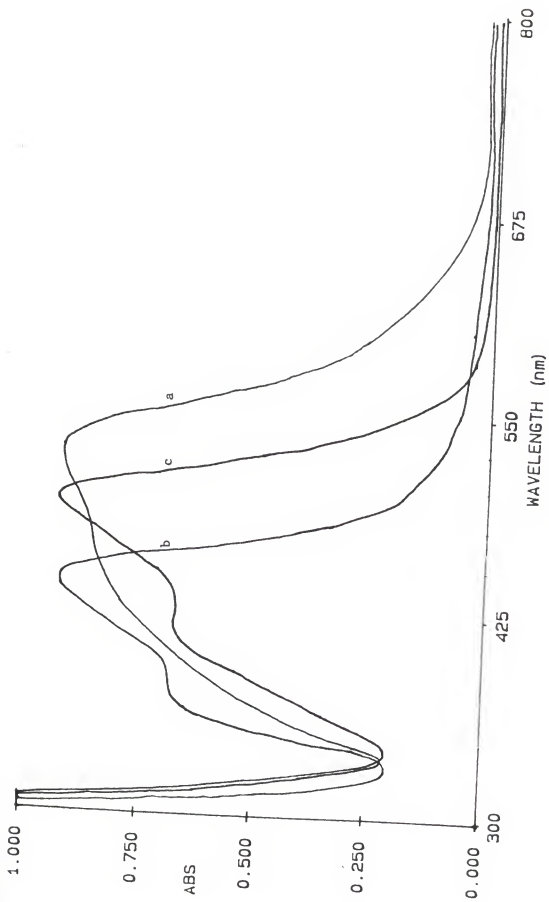
Figure 3-2    ¹H NMR of *cis*-[Ru(dmp)$_2$(NCH$_3$)$_2$](PF$_6$)$_2$.
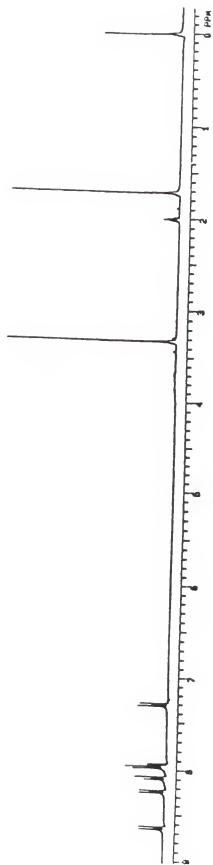
phenanthroline.[51] To determine which resonances to assign to the ring protons, spin decoupling[68] and nuclear overhauser effect (NOE)[69] experiments were carried out. These techniques were performed by irradiating a particular peak and determining which resonance corresponded to the adjacent protons. Using these experimental techniques, the assignments illustrated in Figure 3-3 were made. A similar ^{1}H NMR spectrum was obtained for the diaquo analogue of this dmp complex. Interestingly, upon comparison of the methyl resonances of the diaquo and bis-acetonitrile complexes, markedly separate signals were observed with differences in their chemical shifts being 1 ppm (1.53, 2.53 ppm vs. 1.71, 3.29 ppm). This is due to the local environment of the methyl groups relative to the ancillary ligands. The ^{1}H NMR of the dichloro complex was unclear due to the partial dissociation of some of the chloride ions.

Single crystal X-ray diffraction data on the bis-acetonitrile complex, $[Ru(dmp)_2(NCCH_3)_2](PF_6)_2$ was also obtained to further support a cis configuration for this complex. This crystal structure is illustrated in Figure 3-4. In this structure it can be seen that the ruthenium center is six coordinate. Furthermore, both the acetonitrile ligands are in the cis position. Due to the bulky methyl groups on the phenanthroline ligands, the formation of a trans complex is unlikely due to the interaction of the methyl groups. Unfortunately the bond lengths and angles obtained from this structure are reported with a high degree of uncertainty due to the disorder encountered with the symmetrical $PF_6^-$ counter ions. The values for the bond lengths and angles are reported
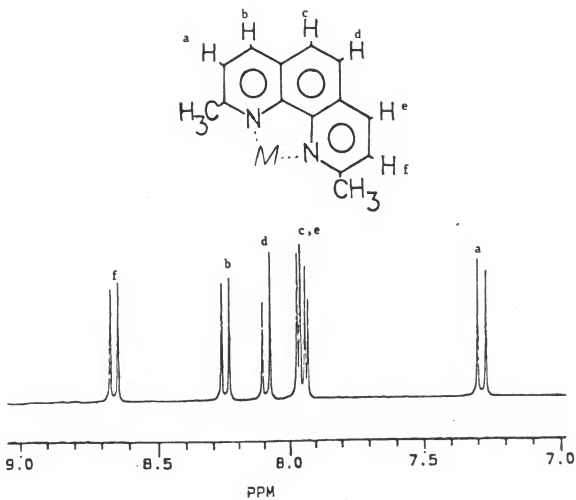
Figure 3-3  $^1$H NMR of Phenanthroline Protons for
*cis*-[Ru(dmp)$_2$(NCCH$_3$)$_2$](PF$_6$)$_2$ in CD$_3$CN.
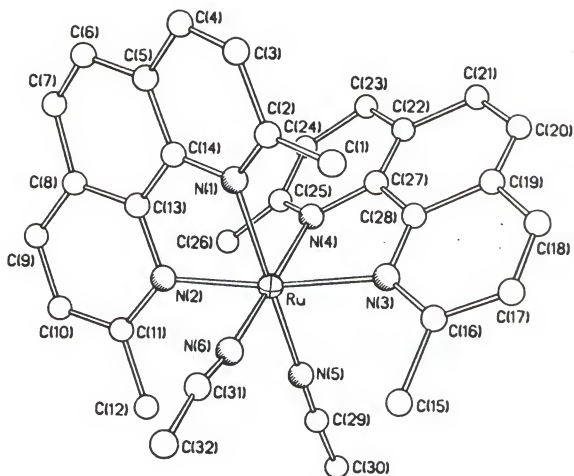
Figure 3-4    X-ray Crystal Structure of *cis*-[Ru(dmp)$_2$(NCCH$_3$)$_2$]$^{2+}$.

Table 3-2
X-ray Crystallographic Data For [Ru(dmp)$_2$(NCCH$_3$)$_2$](PF$_6$)$_2$--Bond Lengths

Bond Lengths (Angstroms)

| | | | | | | |
|---|---|---|---|---|---|---|
| Ru | N1 | 2.142 | | C6 | C5 | 1.422 |
| Ru | N2 | 2.085 | | C6 | C7 | 1.235 |
| Ru | N3 | 2.094 | | | | |
| Ru | N4 | 2.092 | | C7 | C6 | 1.235 |
| Ru | N5 | 2.050 | | C7 | C8 | 1.503 |
| Ru | N6 | 2.063 | | | | |
| | | | | C8 | C7 | 1.503 |
| N1 | Ru | 2.142 | | C8 | C9 | 1.413 |
| N1 | C2 | 1.315 | | C8 | C13 | 1.452 |
| N1 | C14 | 1.381 | | | | |
| | | | | C9 | C8 | 1.413 |
| N2 | Ru | 2.085 | | C9 | C10 | 1.418 |
| N2 | C11 | 1.372 | | | | |
| N2 | C13 | 1.385 | | C10 | C9 | 1.418 |
| | | | | C10 | C11 | 1.418 |
| N3 | Ru | 2.094 | | | | |
| N3 | C16 | 1.319 | | C11 | N2 | 1.372 |
| N3 | C28 | 1.357 | | C11 | C10 | 1.418 |
| | | | | C11 | C12 | 1.497 |
| N4 | Ru | 2.092 | | | | |
| N4 | C25 | 1.353 | | C12 | C11 | 1.497 |
| N4 | C27 | 1.388 | | | | |
| | | | | C13 | N2 | 1.385 |
| N5 | Ru | 2.050 | | C13 | C8 | 1.452 |
| N5 | C29 | 1.145 | | C13 | C14 | 1.378 |
| | | | | | | |
| N6 | Ru | 2.063 | | C14 | N1 | 1.381 |
| N6 | C31 | 1.099 | | C14 | C5 | 1.405 |
| | | | | C14 | C13 | 1.378 |
| C1 | C2 | 1.453 | | | | |
| | | | | C15 | C16 | 1.608 |
| C2 | N1 | 1.315 | | | | |
| C2 | C1 | 1.453 | | C16 | N3 | 1.319 |
| C2 | C3 | 1.449 | | C16 | C15 | 1.608 |
| | | | | C16 | C17 | 1.421 |
| C3 | C2 | 1.449 | | | | |
| C3 | C4 | 1.365 | | C17 | C16 | 1.421 |
| | | | | C17 | C18 | 1.375 |
| C4 | C3 | 1.365 | | | | |
| C4 | C5 | 1.376 | | C18 | C17 | 1.375 |
| | | | | C18 | C19 | 1.408 |
| C5 | C4 | 1.376 | | | | |
| C5 | C6 | 1.422 | | C19 | C18 | 1.408 |
| C5 | C14 | 1.405 | | C19 | C20 | 1.292 |
| | | | | C19 | C28 | 1.520 |

Table 3-2 (continued)

Bond Lengths(Angstroms)

| | | |
|---|---|---|
| C20 | C19 | 1.292 |
| C20 | C21 | 1.368 |
| C21 | C20 | 1.368 |
| C21 | C22 | 1.521 |
| C22 | C21 | 1.521 |
| C22 | C23 | 1.482 |
| C22 | C27 | 1.342 |
| C23 | C22 | 1.482 |
| C23 | C24 | 1.439 |
| C24 | C23 | 1.439 |
| C24 | C25 | 1.390 |
| C25 | N4 | 1.353 |
| C25 | C24 | 1.390 |
| C25 | C26 | 1.494 |
| C26 | C25 | 1.494 |
| C27 | N4 | 1.388 |
| C27 | C22 | 1.342 |
| C27 | C28 | 1.382 |
| C28 | N3 | 1.357 |
| C28 | C19 | 1.520 |
| C28 | C27 | 1.382 |
| C29 | N5 | 1.145 |
| C29 | C30 | 1.409 |
| C30 | C29 | 1.409 |
| C31 | N6 | 1.099 |
| C31 | C32 | 1.538 |
| C32 | C31 | 1.538 |

Table 3-3
X-ray Crystallographic Data For $[Ru(dmp)_2(NCCH_3)_2](PF_6)_2$--Bond Angles

Bond Angles (Degrees)

| | | | |
|---|---|---|---|
| N1-Ru-N2 | 79.3 | C4-C5-C6 | 120.5 |
| N1-Ru-N3 | 94.9 | C4-C5-C14 | 119.5 |
| N1-Ru-N4 | 85.1 | C6-C5-C14 | 120.0 |
| N1-Ru-N5 | 174.4 | | |
| N1-Ru-N6 | 89.6 | C5-C6-C7 | 117.9 |
| | | | |
| N2-Ru-N3 | 172.4 | C6-C7-C8 | 129.0 |
| N2-Ru-N4 | 95.3 | | |
| N2-Ru-N5 | 98.0 | C7-C8-C9 | 128.4 |
| N2-Ru-N6 | 87.2 | C7-C8-C13 | 110.9 |
| | | C9-C8-C13 | 119.5 |
| N3-Ru-N4 | 79.2 | | |
| N3-Ru-N5 | 87.3 | C8-C9-C10 | 117.5 |
| N3-Ru-N6 | 97.8 | | |
| | | C9-C10-C11 | 121.6 |
| N4-Ru-N5 | 90.3 | | |
| N4-Ru-N6 | 173.6 | N2-C11-C10 | 120.2 |
| | | N2-C11-C12 | 120.6 |
| N5-Ru-N6 | 95.1 | C10-C11-C12 | 118.8 |
| | | | |
| Ru-N1-C2 | 130.5 | N2-C13-C8 | 120.2 |
| Ru-N1-C14 | 108.0 | N2-C13-C14 | 118.8 |
| C2-N1-C14 | 120.9 | C8-C13-C14 | 121.1 |
| | | | |
| Ru-N2-C11 | 130.3 | N1-C14-C5 | 120.7 |
| Ru-N2-C13 | 109.6 | N1-C14-C13 | 118.2 |
| C11-N2-C13 | 120.0 | C5-C14-C13 | 120.9 |
| | | | |
| Ru-N3-C16 | 133.8 | N3-C16-C15 | 115.8 |
| Ru-N3-C28 | 108.2 | N3-C16-C17 | 124.9 |
| C16-N3-C28 | 118.0 | C15-C16-C17 | 118.9 |
| | | | |
| Ru-N4-C25 | 128.4 | C16-C17-C18 | 115.7 |
| Ru-N4-C27 | 111.4 | | |
| C25-N4-C27 | 119.8 | C17-C18-C19 | 125.4 |
| | | | |
| Ru-N5-C29 | 177.2 | C18-C19-C20 | 123.5 |
| | | C18-C19-C28 | 111.8 |
| Ru-N6-C31 | 172.1 | C20-C19-C28 | 124.4 |
| | | | |
| N1-C2-C1 | 123.1 | C19-C20-C21 | 120.7 |
| N1-C2-C3 | 118.6 | | |
| C1-C2-C3 | 117.8 | C20-C21-C22 | 118.0 |
| | | | |
| C2-C3-C4 | 121.1 | C21-C22-C23 | 120.2 |
| | | C21-C22-C27 | 119.6 |

Table 3-3 (continued)

Bond Angles(Degrees)

| | |
|---|---|
| C22-C23-C24 | 112.6 |
| C23-C24-C25 | 124.6 |
| N4-C25-C24 | 118.6 |
| N4-C25-C26 | 125.5 |
| C24-C25-C26 | 115.6 |
| N4-C27-C22 | 123.6 |
| N4-C27-C28 | 113.1 |
| C22-C27-C28 | 122.9 |
| N3-C28-C19 | 122.8 |
| N3-C28-C27 | 122.8 |
| C19-C28-C27 | 114.3 |
| N5-C29-C30 | 173.9 |
| N6-C31-C32 | 170.2 |

in Tables 3-2 and 3-3. In a typical X-ray crystal structure the uncertainty of the bond lengths and angles are expressed by the value of R (the smaller the value of R, the more accurate the structure). For this complex a value of R = 12% was obtained due to the disorder of the counter ion. Attempts to obtain crystals using other non-symmetrical anions has been unsuccessful. Although the R value is high for this structure, the geometry of the complex can confidently be assigned to a cis configuration. Attempts to obtain crystal of the diaquo complex were recently successful. In this complex the non-symmetrical acetate ion was used in place of the $PF_6^-$. The crystal structure of this complex has not yet been determined.

To determine if the formation of a 1-oxo dimer is feasible using this sterically hindered ruthenium complex, the crystallographic coordinates from the structure of an 1-oxo iron-phenanthroline dimer[70] were used to make a model. The coordinates of this structure were modified slightly with the addition of the methyl groups on the 2,9 position of the phenanthroline ring. These coordinates were placed into a molecular mechanics program that would simulate this dmp dimer. This is illustrated in Figure 3-5. In this modeled complex, if distance of the methyl groups on adjacent metal centers is measured, the distance between these methyl groups is less then 2.0 A. This indicates that the formation of a 1-oxo dimer is unlikely.

A variety of spectroscopic methods were also used to characterize the high valent Ru(IV)O and Ru(VI)(O)$_2$ complexes. Infrared spectroscopy is often used to characterize or identify metal-oxo complexes due to the distinct metal-oxo stretching frequency. In this case IR was

Figure 3-5    Model Structure of $[Ru(dmp)_2(S)]_2O$
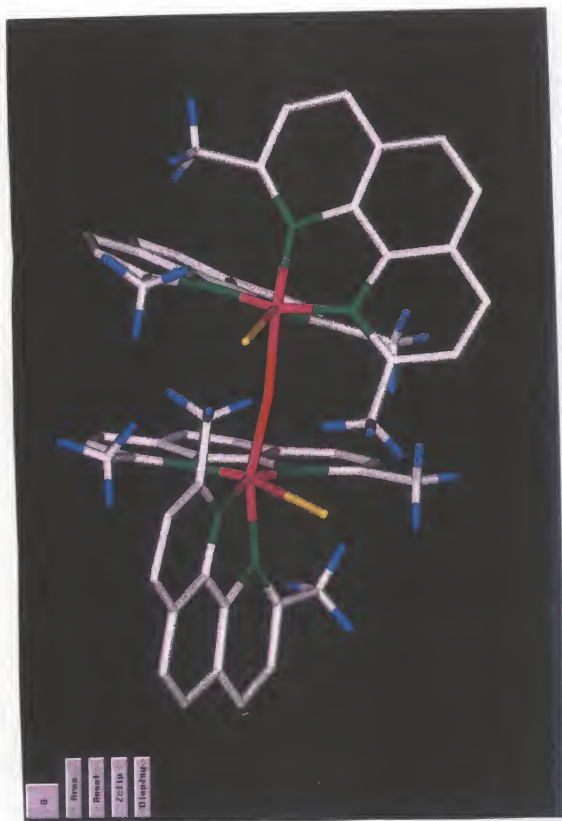
unsuccessful due to the interference of the P-F stretching frequency from the $PF_6^-$ counter ion. Substraction of the P-F stretch also proved to be unsuccessful.

A series of UV/visible experiments were carried out to characterize the high valent ruthenium-oxo complexes. These experiments are illustrated in Figure 3-6. These spectra illustrate the changes which accompany the diaquo complex, $[Ru(dmp)_2(OH_2)_2]PF_6]_2$ as function of addition of a 10% aqueous $H_2O_2$ solution. Similar changes are also observed upon addition of aqueous $H_2O_2$ using the bis-acetonitrile complex, $[Ru(dmp)_2(NCCH_3)_2](PF_6)_2$. It can be seen that as $H_2O_2$ is added to the Ru(II) complexes, in 0.5 equivalent intervals, a variety of spectral changes are observed, with the formation several distinct isosbestic points. The initial curve (a), is the Ru(II) complex in distilled water. Upon addition of $H_2O_2$, the formation of an isosbestic point at 395 nm is observed. This point has been assigned to the oxidation of the ruthenium(II) to ruthenium(III). A decrease in absorption at 490 nm and an increase in absorption at 365 is observed. Upon further addition of $H_2O_2$, this isosbestic point at 395 nm is lost. From 3.0 to 4.5 equivalents of $H_2O_2$ a second isosbestic point is observed at 425 nm. This isosbestic point is assigned to the oxidation of the ruthenium(III) to ruthenium(IV). These spectral changes are similar to those observed by Meyer[67,71] for the formation of Ru(IV)O species by oxidation of $[Ru(bpy)_2(py)](ClO_4)_2$ with Ce(IV). The 425 nm isosbestic point disappears upon addition of a total of 7 equivalents of $H_2O_2$ (curve n). This is attributed to the formation of $Ru(VI)(O)_2$ species. This curve fortuitously passes through a common point at 425

Figure 3-6    UV/Visible Spectra of *cis*-[Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$ with Addition of H$_2$O$_2$ in 0.5 Equivalent Intervals.
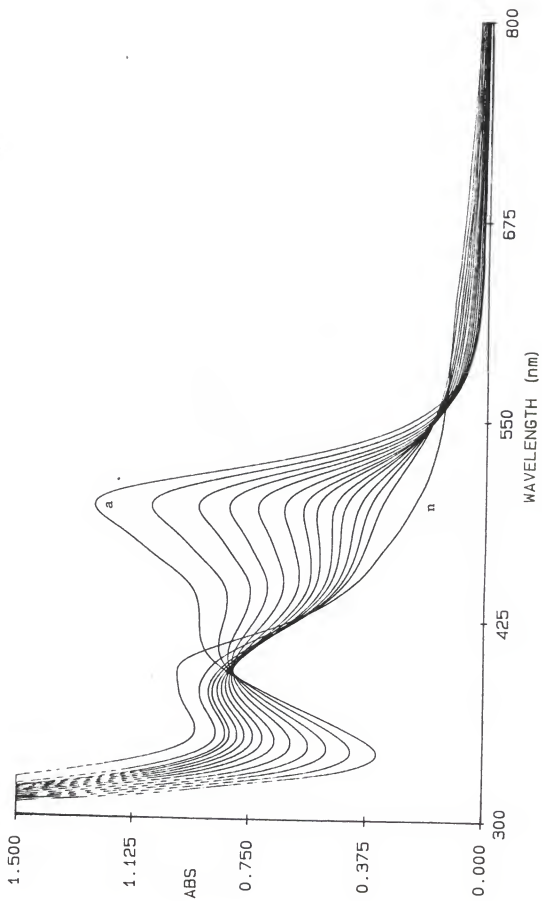
nm. This is one of very few cases in which $H_2O_2$ has been shown to be capable of oxidizing a Ru(II) species to a higher valent oxo complex. The only report in which $H_2O_2$ is used as an oxidant to generate high valent ruthenium-oxo complexes has been demonstrated by Che and co-workers[72]. In this work, $H_2O_2$ is reported to be used to oxidize several different ruthenium(II) macrocycle complexes to higher valent oxo species. One of these reported tertiary amine compounds, Ru(II)(16-TMC) (1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) is shown to be oxidized using $H_2O_2$ to the high valent trans-Ru(VI)(O)$_2$ species. In most cases, the oxidizing agent used to generate ruthenium-oxo complexes is cerium(IV). One reason for using this oxidant, rather than $H_2O_2$, is that the metal complex decomposes some of the $H_2O_2$, making the exact quantity needed to generate the oxo complexes more difficult to determine. Cerium on the other hand, is a one electron oxidant and can be used without any side reactions, such as decomposition. The use of cerium(IV) was not used in our case, to eliminate any possibility of cerium impurities in the final product. Bailey suspected that one possible problem in the isolation of a pure high valent cis-[Ru(VI)(O)$_2$(dmp)$_2$](PF$_6$)$_2$ was due to cerium impurities.

To further support the formation of these high valent mono-oxo and dioxo species, a series of [1] NMR experiments were performed. As illustrated in Figure 3-7, a typical ^{1}H NMR spectrum of [Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$ covers a range of 10 ppm. Characteristics of this spectrum were discussed above. With the addition of 3 equivalents of $H_2O_2$, as illustrated in Figure 3-8, a spectrum with chemical shifts ranging from +60 ppm to -20 ppm results. These isotropic shifts are

Figure 3-7    $^1$H NMR of *cis*-[Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$.
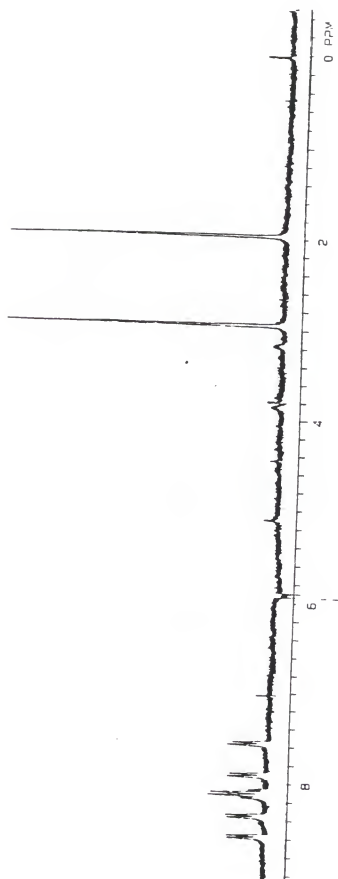
Figure 3-8    $^1$H NMR of *cis*-[Ru(dmp)$_2$(OH$_2$)$_2$]$^{2+}$](PF$_6$)$_2$ After the Addition of 3 Equivalents of H$_2$O$_2$.

characteristic of a paramagnetic species. Groves and co-workers have observed similar shifts in their oxidized *trans*-ruthenium porphyrin system,[56] and in their iron porphyrin complexes.[73] These complexes have been characterized as the $[Ru(IV)O]^{2+}$ and $[Fe(IV)O]^{2+}$ species. It is speculated that the species being formed with the addition of 3 equivalents of $H_2O_2$ is the ruthenium(IV) oxo species or a mixture of the ruthenium(III) and (IV). This equilibrium between Ru(III) and Ru(IV) is illustrated in equation 3-1.

$$Ru \overset{\displaystyle \overset{H}{\underset{}{O-H}}}{\underset{O-H}{}} \quad \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \quad Ru \overset{\displaystyle \overset{H}{\underset{}{O-H}}}{\underset{O}{}} \qquad \text{Equation 3-1}$$
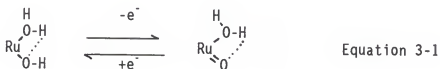
To determine which of these broad resonances correspond to the methyl groups on the phenanthroline ligands, a series of T1 NMR experiments were performed. In these experiments, the methyl groups are expected to have the shortest T1's since they are the closest to the paramagnetic ruthenium center.[69] These experiments are illustrated in Figure 3-9. In these experiments the peak at 55.95 ppm has the shortest T1. This peak should be the methyl groups on the phenanthrolines, which are the closest to the paramagnetic metal center. If these contact shifts are compared to those reported by La Mar[74], as well as DeSimone[75] for a variety of Fe(III) phenanthroline complexes, the substituents at the 2,9 positions should be shifted upfield from that seen for the Ru(II)

Figure 3-9    T1 Experiments of *cis*-[Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$ After the Addition of 3 Equivalents of H$_2$O$_2$.
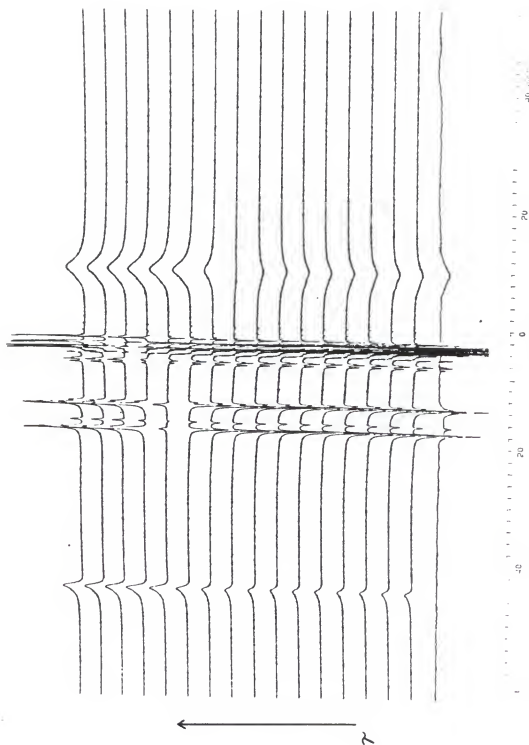
precursor. Ruthenium should be similar to iron in that the unpaired spin density should be placed into the p system of the ligand system. In La Mars' work, the protons on the 2,9 positions of phenanthroline are shifted upfield. Upon substitution of different protons by methyl groups, La Mar observes shifts in the same direction as those observed for the unsubstituted position. If methyl groups are substituted at the 2,9 positions, as in our case, the methyl protons will also be shifted upfield. Therefore, based on this analogy, the methyl groups are the upfield resonance at -11.93 ppm. Due to the broadness of this peak only one resonance from the methyl groups is observed. The remaining downfield resonances are caused by the remaining protons on the dmp ligand. These assignments are only tentative and deuterium substitution experiments would have to be performed to make any definite assignments. A listing of the various relaxation time values are listed in Table 3-4.

Upon further addition of $H_2O_2$ to the above paramagnetic species, the $^1H$ NMR spectrum dramatically changes back to a spectrum characteristic of a diamagnetic species. As illustrated in Figure 3.10, the phenanthroline region for this species is very similar to that of the percursor, $[Ru(dmp)_2)(OH_2)_2](PF_6)_2$. All of the resonances observed in the Ru(II) complexes are also present in this oxidized species, indicating that the rings still are intact. There is a slight loss of resolution in the spectrum due to the presence of $H_2O$ from the added peroxide. These resonances are however shifted slightly downfield, due to the shielding effect of the oxo groups which are bound in a cis fashion to the metal center. This complex is being assigned to the high

Figure 3-10    $^1$H NMR of *cis*-[Ru(dmp)$_2$(OH$_2$)$_2$](PF$_6$)$_2$ After
Addition of 7 Equivalents of H$_2$O$_2$.

[Ru(DMP)₂(OH₂)₂](PF₆)₂

[Ru(DMP)₂(OH₂)₂](PF₆)₂ + 7 H₂O₂

PPM
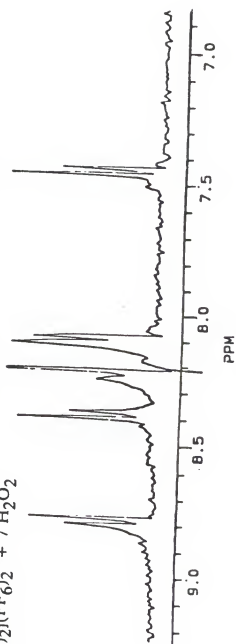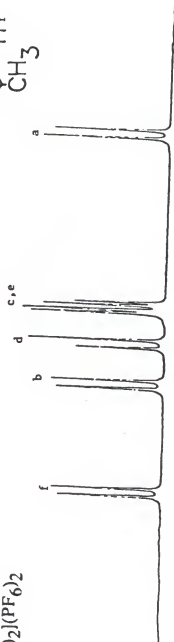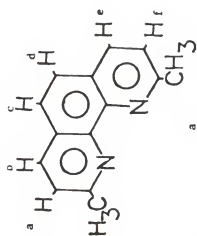
valent dioxo complex, $[Ru(VI)(O)_2(dmp)_2](PF_6)_2$. This $d^2$ complex, as well as other cis-dioxo ruthenium species are believed to be diamagnetic, explaining the change observed in the $^1H$ NMR spectrum. Based on these experiments, the addition of 3 equivalents of $H_2O_2$ results in the formation of the Ru(IV)O species, and the addition of 7 equivalents of $H_2O_2$ results in the Ru(VI)(O)$_2$ species. The need for more than the expected 2 or 4 equivalents of this oxidant was due to the decomposition of the $H_2O_2$ by the metal complex, as described in Chapter 2. Furthermore, these spectral changes are also observed using OCl$^-$ as an oxidant, indicating metal-oxo species are being formed and ruling out the formation of metal-peroxide complexes.

Table 3-4
Relaxation Values From T1 Experiment of $[Ru(IV)O(dmp)_2(OH_2)](PF_6)_2$

| Peak (ppm) | T1 (sec) | Error (sec) |
|---|---|---|
| 55.95 | $6.49 \times 10^{-5}$ | $1.1 \times 10^{-7}$ |
| 21.99 | $5.82 \times 10^{-3}$ | $2.2 \times 10^{-5}$ |
| 16.87 | $4.84 \times 10^{-2}$ | $3.2 \times 10^{-5}$ |
| 7.59 | $1.40 \times 10^{-2}$ | $1.2 \times 10^{-4}$ |
| 6.00 | $4.00 \times 10^{-2}$ | $2.0 \times 10^{-4}$ |
| 5.24 | $4.32 \times 10^{-2}$ | $3.2 \times 10^{-4}$ |
| 5.01 | $4.41 \times 10^{-2}$ | $5.0 \times 10^{-5}$ |
| 3.92 | $6.12 \times 10^{-2}$ | $4.2 \times 10^{-5}$ |
| 2.82 | $2.33 \times 10^{-2}$ | $2.3 \times 10^{-4}$ |
| -11.93 | $2.42 \times 10^{-4}$ | $3.4 \times 10^{-6}$ |

CHAPTER 4

## THE OXIDATION OF OLEFINS BY RUTHENIUM
## DIMETHYL PHENANTHROLINE COMPLEXES

### Introduction

The oxidation of various hydrocarbons to oxygenated products was outlined in Chapter 1. The epoxidation of olefins is an important industrial process. Olefinic substrates were initially investigated by the rubber industry as autoxidation substrates.[19] This led to the current process for the epoxidation of ethylene and the Wacker process. Due to the lack of any feasible liquid phase oxidation process for the epoxidation of propylene, a great deal of effort has concentrated on the selective oxidation of olefins.[76]

Ethylene and propylene are commercially inviting substrates, due to the demand of their respective epoxides for plastics, solvents, antifreeze, and other chemicals.[33] The epoxidation of ethylene over a silver-alumina catalyst is a well-studied heterogeneous system.[4,77-80] Propylene, on the other hand, can not be epoxidized under similar conditions and is currently epoxidized using a molybdenum-catalyzed process in the presence of an alkylhydroperoxide.[19,78] In 1987, 5.62 billion pounds of ethylene oxide and 2.61 billion pounds of propylene oxide were produced in the United States.[81]

Asymmetric epoxidations have also received a great deal of attention in the literature due to Sharpless' discovery that chiral

titanium -isopropoxide complexes catalyze the epoxidation of allylic alcohols.[45,82-85] Epoxides formed in this manner are generally greater than 95% enantiomerically pure. This process has recently been licensed by Aldrich Chemical Company and can be used to prepare intermediates for an assortment of natural products of interest to the pharmaceutical industry.[86]

## Background

Metal-oxo reagents, most commonly containing molybdenum or vanadium, in combination with peroxides or hydroperoxides, have been shown to actively epoxidize olefins.[29] The mechanism involved in the peroxomolybdenum-catalyzed epoxidation of olefins is the center of a great deal of controversy. Both Sharpless and Mimouns' mechanisms are referred to for these and related oxidations.[11,13,29,87]

The epoxidation of olefins using the enzyme cytochrome P-450 and its inorganic porphyrin analogues has been the focus of an extensive amount of research.[88-92] The mechanisms by which this enzyme oxidizes organic compounds have also been an area of much attention.[88,89] This is because the active center of this enzyme is thought to be a metal-oxo moiety. Groves and co-workers reported that $Fe^{III}(TPP)Cl/PhIO$ (TPP = tetraphenyl porphyrin) is capable of performing chemistry similar to that of cytochrome P-450.[93] This has fostered much research into the proposed iron-oxo reactive intermediate.[94] These iron-oxo intermediates are known to be catalysts which epoxidize olefins via an oxygen atom transfer mechanism.[95] As previously mentioned, the thermal instability of these highly reactive iron-oxo centers makes them difficult to work

with. The periodic relationship of iron and ruthenium suggests that the latter could provide stable examples of metal-oxo complexes.

High valent ruthenium-oxo complexes have received considerable attention because of the potential of these species as catalysts for the oxidation of a variety of organic functional groups.[51,59,72,96-100] The reason for studying ruthenium as the metal center for these systems is that there is a wide range of oxidation states which are readily accessible to the ruthenium center.[101] This makes ruthenium very attractive as a potential catalyst. Of particular interest are ruthenium complexes containing polypyridyl ligands whose structures provide a means of both stabilizing higher oxidation states and imparting stability to the complex.

Meyer and co-workers have extensively studied[67,97,99-102] $[Ru(IV)O(bpy)_2(py)](ClO_4)_2$ (bpy = bipyridine, py = pyridine) as an oxidation catalyst for a variety of organic substrates. This complex has been shown to oxidize olefins stoichiometrically to the corresponding epoxide.[100] In this reaction an oxygen atom transfer reagent, such as $NaIO_4$ is needed to regenerate the active ruthenium(IV)oxo species after oxygen atom transfer to the olefin. Both styrene and norbornene are oxidized to the corresponding epoxide, where cyclohexene is oxidized to the allylic products, 2-cyclohexen-1-one, 2-cyclohexen-1-ol and cyclohexene epoxide. These allylic products are common for the oxidation of cyclohexene. In these reactions, loss of activity is encountered over time which has been attributed to the formation of 1-oxo dimers.[103] Once formed, these dimers lead to inactive catalyst. Meyer has also studied[104] the reactivity of

[Ru(IV)O(trpy)(bpy)](ClO$_4$)$_2$ (trpy = terpyridine). This complex has shown comparable activity and ability to oxygen atom transfer to the bis-bpy complex.

Takeuchi and co-worker[105] have taken this work one step further by substituting a phosphine ligand in place of the pyridine ligand, [Ru(IV)O(bpy)$_2$(PR$_3$)](ClO$_4$)$_2$. This complex also is capable of oxidizing olefins stoichiometrically. The active high valent Ru(IV)O species is regenerated using an oxygen atom transfer reagent such as hypochlorite or iodosobenzene. This catalyst system has demonstrated the capability of aerobically oxidizing cyclohexene.[106] In these oxidations, low conversions were observed over the 24 hour reaction time with the product ratio of 14 : 7 : 1 corresponding to 2-cyclohexen-1-one : 2-cyclohexen-1-ol : cyclohexene epoxide. This ruthenium (IV) complex has also demonstrated the ability to oxidize primary alcohols stoichiometrically.[107] Again loss of activity is observed suggesting problems of the formation of $\mu$-oxo dimers. In both the work by Meyer and Takeuchi, the formation of the high valent dioxo are not achieved due to the axial bound ligands. These complexes have been shown primarily to be stoichiometric or electrocatalytic oxidants.

The area of ruthenium dioxo chemistry has also attracted much attention. Che and co-workers have reported the aerobic oxidation of alcohols using a *trans*-Ru(VI)(O)$_2$ tertiary amine complex.[108] In this work the *trans*-Ru(O)$_2$(16-TMC) (16 TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) was shown to be capable of aerobically oxidizing benzyl alcohol to benzaldehyde at room temperature. This system proceeded with 2.5 turnovers/18 hours (turnover = mole product/

mole catalyst). Again problems with the formation of 1-oxo dimers are a possible explanation of the loss of activity. Che has overcome this problem of dimer formation in a report[109] in which he uses a chlorinated ruthenium complex, cis-[Ru(VI)(O)$_2$(6,6' Cl$_2$bpy)$_2$]$^{2+}$ as an oxidation catalyst. As mentioned in Chapter 3, the isolation of unstable cis-Ru(VI)(O)$_2$ complexes is difficult, but cis-Ru(VI)O$_2$ complexes have been isolated by Che. The cis-dioxo complex is an extremely potent oxidant, much more potent then the previously mentioned trans-dioxo species. The reaction with chloride results in the rapid production of Cl$_2$. This Ru(VI)(O)$_2$ species also oxidizes olefins primarily to the epoxides. Once again in these reactions an oxygen atom transfer reagent, or Ce(IV) is necessary to regenerate the active Ru(VI)(O)$_2$ species. The use of this sterically hindered complex has been shown to prevent the formation of 1-oxo dimers, leading to an increase in the catalyst lifetime.

To overcome the recurring problem of the formation of 1-oxo dimers, Groves and co-workers[96] have also reported the use of a sterically hindered ligand system. In this work, the trans-Ru(VI)(O)$_2$(TMP) system (TMP = 5,10,15,20-tetramesitylporphyrin) was shown to aerobically epoxidize alkenes. Due to the steric hindrance caused around the O=Ru=O moiety by the mesityl groups, the formation of the inactive 1-oxo dimers can be prevented. This complex has been shown to selectively oxidize a variety of olefins under mild reaction conditions of 25°C and 3 atmospheres O$_2$. This is the first report in which an active high valent ruthenium-oxo complex could be regenerated using O$_2$.

Bailey has reported[59] that the sterically hindered high valent ruthenium complex, cis-[Ru(O)$_2$(dmp)$_2$](PF$_6$)$_2$ was capable of selectively

oxidizing olefins under aerobic conditions. This ligand system was selected for two reasons. First, due to the bulky methyl groups on the phenanthroline ligand, the formation of $\mu$-oxo dimers should not be a problem. Second, this ligand system is neutral, causing the formation of a more electro-positive metal center, which should increase its activity. In this preliminary report, this high valent complex was shown to oxidize norbornene to the corresponding norbornene oxide (37 turnovers/48 hours) and styrene was shown to be oxidized to a mixture of benzaldehyde (7 turnovers/48 hours) and styrene oxide (not quantified). These reactions were carried out at 55°C and 3 atmospheres $O_2$.

One characteristic of these reactions which was not understood was the presence of a 24 hour induction period before the formation of products were observed. Experiments were performed to determine the cause. In this experiment, norbornene was reacted with $O_2$ under the reaction conditions in the absence of the catalyst, for 24 hours, the time of the induction period. After this time the catalyst was added to the reaction mixture. A 24 hour induction period still was observed indicating the formation of an alkylhydroperoxide was not the cause of the 24 hour induction period. Based on these experimental results, it was concluded that the catalyst being used in this reaction is a catalyst precursor to the active catalytic species. This raises to question of whether the $cis$-Ru(O)$_2$ complex was actually the original starting material.

As previously mentioned, the formation of $cis$-dioxo complexes of ruthenium is thermally instable, making the isolation of this complex extremely difficult. This led us to study the potential catalytic

activity of the precursor to this high valent ruthenium complex,
$[Ru(II)(dmp)_2(S)_2](PF_6)_2$ (S = $H_2O$ or $CH_3CN$).

Upon comparison of the oxidation potentials of several the
ruthenium complexes described above, and related systems, which have
been shown to be capable of oxidizing organic substrates, it is
remarkable how similar these potentials are. A listing of some of these
oxidation potentials is illustrated in Table 4-1. Many of these
compounds demonstrate quite different reactivity for the oxidation of
organic substrates. This indicates, since the oxidation potentials of
these complexes are similar, that the difference in the activity of
these complexes must be a kinetic effect.

## Scope of Catalysis

The general setup and apparatus used are the same as that described
in Chapter II in the section "Scope of Catalysis." For the olefin
oxidations, the reactions were carried out at 65°C; all the reactions
were performed under 40 psi $O_2$ initial pressure. Except where otherwise
noted, the solvent in these reactions was acetonitrile. In all cases a
minimum of a 100-fold excess of substrate was used. The products in the
reactions were analyzed and quantified via GC and/or GC-MS. The
procedure used varied depending on the substrate studied. For
norbornene, a solid, the substrate was dissolved in 50 mL of
acetonitrile in the pressure bottle. Upon dissolution of the solid, the
catalyst was added to the solution and the apparatus assembled. The
norbornene was used as received; however for some of the liquid

Table 4-1

Oxidation Potentials for Ruthenium Complexes

| Compound | III/II | IV/II | IV/III | VI/IV | Solvent |
|---|---|---|---|---|---|
| $Ru(dmp)_2(OH_2)_2^{2+}$ | 0.72 | 0.89 | 1.06 | 1.24 | $HBF_4^{69}$ |
| $Ru(TMP)(CO)$ | 0.60 | 0.84 | 1.08 | 1.12 | $CH_2Cl_2^{51}$ |
| $Ru(TPP)(CO)$ | --- | 0.85 | --- | 1.26 | $CH_2Cl_2^{133}$ |
| $Ru(bpy)_2(py)^{2+}$ | 0.78 | 0.89 | 0.99 | --- | $HClO_4^{102}$ |
| $Ru(bpy)_2(OH_2)_2^{2+}$ | 0.72 | 0.87 | 1.10 | 1.45 | $HBF_4^{69}$ |
| $Ru(biq)_2(OH_2)(PEt_3)^{2+}$ | 0.75 | 0.82 | 0.91 | --- | $HClO_4^{110}$ |

substrates used, pretreatment by washing through a neutral alumina
column to remove peroxides was required. In the case of cyclohexene, 10
mL of substrate was added to 40 mL of acetonitrile. Other reactions
were carried out by adding 3 mL of substrate to 47 mL of acetonitrile.
No internal standard was used in any of these reactions, except 2-
octanone in the oxidation of cyclohexene. In a typical reaction $10^{-5}$
moles of catalyst was used. Products determined by GC, were carried out
using a DEGS column and an FID detector. The quantity of products
formed was determined from a calibration curve relating moles of
products to the relative area percent as described in Chapter 2.

## Results and Discussion

Due to the thermal instability and our inability to isolate the
high valent $cis$-[Ru(VI)(O)$_2$(dmp)$_2$](PF$_6$)$_2$, alternative methods for
investigating the reactivity and mechanism of the epoxidation reaction
reported by Bailey[59] were sought. This was achieved by studying the
catalytic activity of the precursor to the high valent dioxo complex.
The synthesis and characterization of this ruthenium (II) compound,
[Ru(II)(dmp)$_2$(S)$_2$](PF$_6$)$_2$ (S = CH$_3$CN or H$_2$O) was discussed in Chapter 3.
The ability for O$_2$ to oxidize Ru(II) complexes to higher valent oxo
species as proposed by Groves[56], Kochi[57] and Collman[58] led us to
investigate this complex for the epoxidation of olefins. These
oxidative addition reactions of O$_2$ and ruthenium(II) complexes were
discussed in Chapter 3.

The oxidation of norbornene was initially attempted using the bis-
acetonitrile complex, [Ru(II)(dmp)$_2$(NCCH$_3$)$_2$](PF$_6$)$_2$ under the reaction

conditions described above. The results of this experiment are illustrated in Figure 4-1. In this plot of time vs. turnovers, where a turnover = mole of product/ mole of catalyst, several interesting reaction characteristics are seen. The reaction proceeds with a 12 hour induction period. This induction period is 1/2 as long as the induction period which was reported by Bailey. Furthermore, the reaction proceeds with 94% selectivity to the epoxide and with 35 turnover/48 hours. In Figure 4-1, the turnover numbers account only for the epoxide. In the reaction, 6% of 2-norbornanone and 2-norbornanol were observed. This is comparable to that observed by Bailey. This oxidation can be carried out using either the bis-acetonitrile or diaquo analogue of the $Ru(II)(dmp)_2$ complex with comparable results.

The nature of the 12 hour induction period was investigated. One explanation is that $O_2$ is oxidatively adding to the Ru(II) complex, to generate a higher valent oxo species. To determine if this is occurring, the catalyst was reacted with $O_2$ in the absence of the substrate for 12 hours, the length of the induction period. This experiment is illustrated in Figure 4-2. Upon addition of the substrate, norbornene, an additional 12 hour induction period was observed. This indicates that $O_2$ alone is not initially generating the active catalyst. An alternative explanation of the induction period is that $O_2$ is reacting with the substrate to generate an alkylhydroperoxide. Once formed this hydroperoxide can decompose to the products. To determine if this is a feasible explanation, the substrate, norbornene was reacted with $O_2$ in the absence of the ruthenium complex for 12 hours, the time of the induction period. This
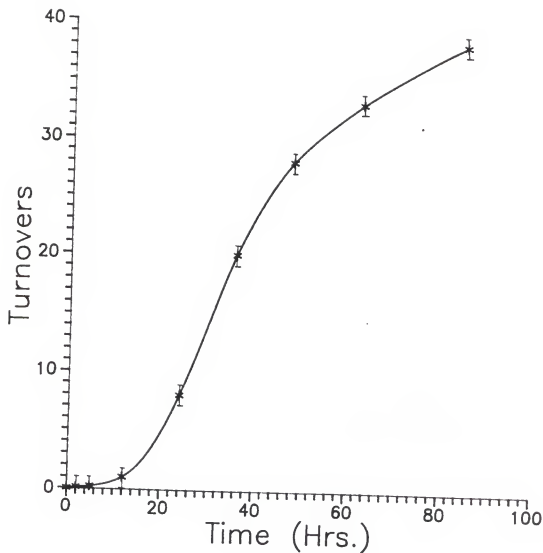
Figure 4-1    The Oxidation of a 0.6 M CH₃CN Solution of Norbornene
              by 2 x 10⁻⁴ M (10⁻⁵ moles) of [Ru(dmp)₂(S)₂](PF₆)₂ at
              65°C and 3 Atmospheres.
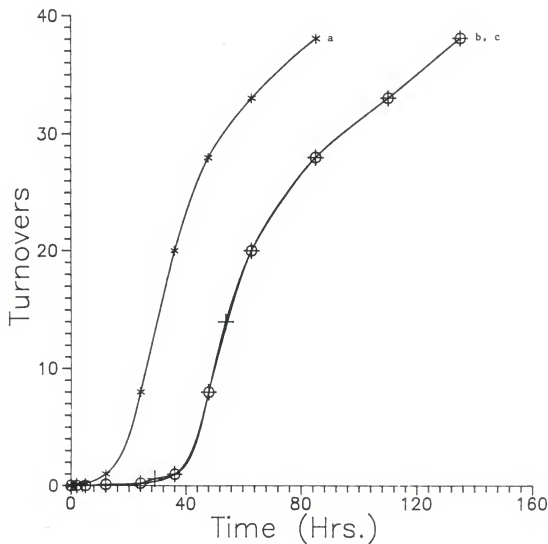
Figure 4-2    Investigation of the Induction Period for the
              Oxidation of Norbornene by $[Ru(dmp)_2(S)_2](PF_6)_2$ at
              65°C and 3 Atmospheres - a) Catalyst + $O_2$ +
              Norbornene, b) Catalyst + $O_2$, c) Norbornene + $O_2$.

experiment is also illustrated in Figure 4-2. After the initial 12 hours, no products were observed. Furthermore, upon addition of the bis-acetonitrile complex, there was still an additional 12 hour induction period before the formation of products was observed. This result is the same as that observed by Bailey. As illustrated in Figure 4-3, upon addition of a small aliquot of t-butylhydroperoxide to the reaction mixture, the induction period was eliminated. Based on these experiment, three components are necessary to initiate this oxidation reaction, the catalyst, substrate and $O_2$. This reaction also seems to be initiated by the formation of an alkylhydroperoxide. The metal complex apparently catalyzes the formation of such a peroxide.

A variety of radical experiments were carried out to determine if this reaction was proceeding via a radical mechanism . These experiments are illustrated in Figure 4-4. The addition of AIBN (a free radical initiator, azo-bis(isobutyronitrile)) to the catalyst mixture did not have a large influence on the catalyst activity. In this experiment however, the induction period was shortened to 4 hours and the selectivity to the epoxide decreased to 89%. Both the alcohol and ketone were the other products observed here. With the addition of benzoquinone, a radical trap, to the reaction mixture, no oxidation was observed for the first 72 hours. After this time the normal product distribution was observed. The formation of products after 72 hours was due to the fact that the radical trap is consumed and the reaction then proceeds as normal. The use of AIBN in the absence of the catalyst did not initiate the oxidation reaction. Based on these experiments, it can
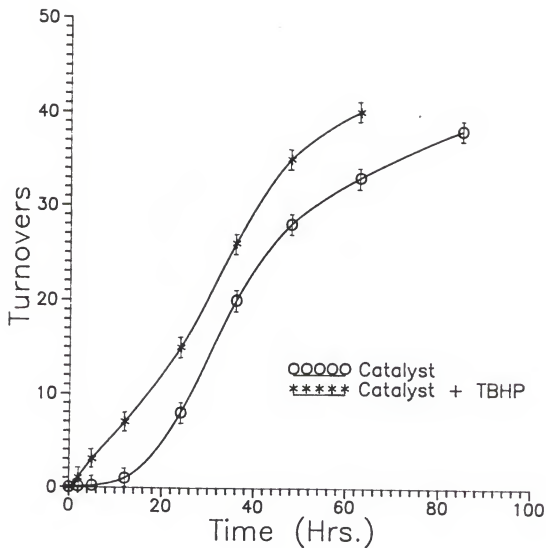
Figure 4-3  Reaction of a 0.2 M Butanol Solution of t-Butylhydroperoxide with a $CH_3CN$ Solution of 0.6 M Norbornene at 65°C and 3 Atmospheres.  The catalyst is $[Ru(dmp)_2(S)_2](PF_6)_2$ $(2 \times 10^{-4}$ M).

Figure 4-4   Free Radical Experiments for the Oxidation
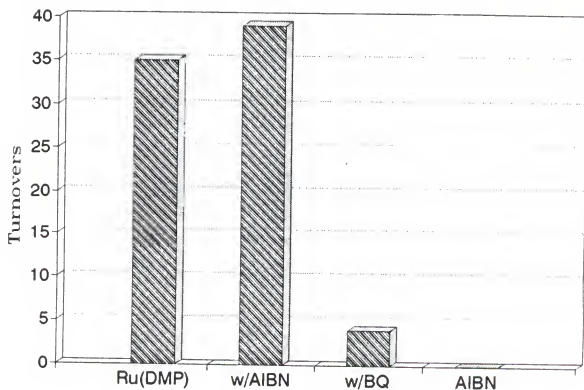            of a 0.6 M $CH_3CN$ Solution of Norbornene by $2 \times 10^{-4}$ M
            ($10^{-5}$ moles) of $[Ru(dmp)_2(S)_2](PF_6)_2$ at 65°C and 3
            Atmospheres.

be concluded that radicals are involved in the induction step of this oxidation reaction.

A proposed mechanism for this epoxidation reaction is illustrated in Figure 4-5. In this mechanism, based on the experiment discussed above, the initial step involves the interaction of the catalyst precursor, $[Ru(II)(dmp)_2(NCCH_3)_2](PF_6)_2$, $O_2$ and the substrate to form a metal-alkylperoxide. This peroxide can decompose forming the $[Ru(IV)O(dmp)_2(NCCH_3)](PF_6)_2$ species, a mole of epoxide and some alcohol and ketone. Mimoun[23] has shown that epoxides can be produced from the decomposition alkylhydroperoxides. This is the source of the alcohol and ketone which is observed in the oxidation reaction. Once formed, the Ru(IV)O species can take one of either 2 possible steps. It can react with the olefin via an oxygen atom transfer reaction to yield the epoxide and generate the Ru(II) starting material. This Ru(II) species then must go through the initiation reaction to regenerate the Ru(IV)O complexes. Alternatively, the Ru(IV)O species can react with $O_2$ in a fast step, relative to the reaction with the olefin, to form the high valent $cis$-$[Ru(VI)(O)_2(dmp)_2](PF_6)_2$ species. This dioxo complex can then oxygen atom transfer to the olefin, yielding the epoxide and the Ru(IV)O species. The Ru(IV)O species then can react with $O_2$ again to generate the dioxo active catalyst. Based on this proposed mechanism, the catalytic cycle occurs between ruthenium(IV) and ruthenium(VI) species.

To further support the proposed mechanism, it was demonstrated in Chapter 3 that peroxides are potent enough oxidants to generate high valent oxo complexes of this substituted ruthenium complex. This supports the initial step of the mechanism, the formation of the Ru(IV)O
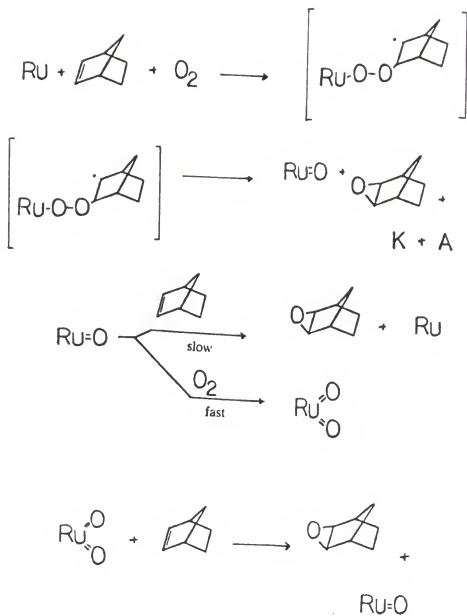
Figure 4-5    Proposed Mechanism for the Oxidation
of Norbornene by [Ru(dmp)$_2$(S)$_2$](PF$_6$)$_2$.

species from the norbornyl-peroxide.

The feasibility of the Ru(IV)O species reacting rapidly with $O_2$, relative to the reaction with the olefin, was investigated. The Ru(IV)O species was generate "in situ" as described in Chapter 3. This was accomplished with the addition of 3 equivalents of $H_2O_2$. The UV/Vis of this species was obtained to determine if the Ru(IV)O species had been generated. Once formed, this complex was used for the epoxidation of norbornene. The results of this experiment are illustrates in Figure 4-6. In this Figure, it can be seen that Ru(IV)O species does react with $O_2$ readily to form an active catalytic species. In this oxidation reaction, the 12 hour induction period previously seen was eliminated. This indicates that the Ru(IV)O is reacting with $O_2$ to form the high valent cis-Ru(VI)(O)$_2$ species. This complex is then oxygen atom transferring to the olefin. To determine if $O_2$ was oxidizing the Ru(IV)O complex to the dioxo, the following experiment was performed. The Ru(IV)O was generated with the addition of 3 equivalents. This complex was the reacted with $O_2$ at 75°C. When monitored by UV/Vis, the observed spectrum lies between that of the Ru(IV)O and Ru(VI)(O)$_2$ species previously observed in Chapter 3. This is illustrated in Figure 4-7. Due to the time involved in obtaining a spectrum of this complex, the partial decomposition may be occurring to the Ru(IV)O and Ru(II) complexes. If this sample is monitored by UV/Vis, within 25 minutes the spectrum looks identical to that of the Ru(IV)O species. This further supports the fact that the Ru(VI)(O)$_2$ species is unstable and decomposes to the Ru(IV)O species. In the above reaction, the selectivity for the epoxidation of norbornene increased to 100%. This further supports the
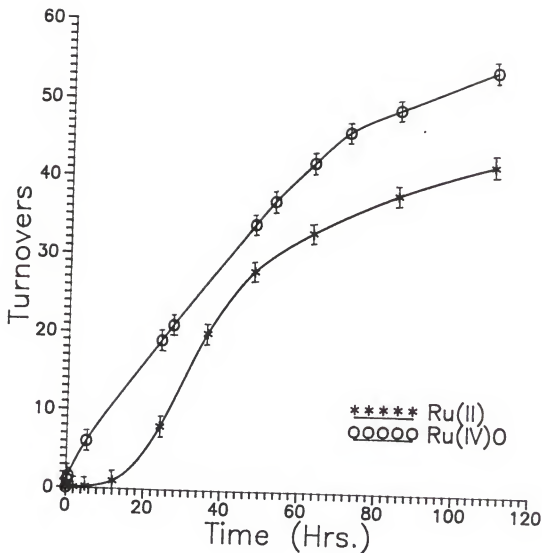
Figure 4-6    Oxidation of a 0.6 M CH₃CN Solution of Norbornene by
              2 x 10⁻⁴ M (10⁻⁵ moles) of [Ru(IV)O(dmp)₂(S)₂](PF₆)₂ at
              65°C and 3 Atmosheres.  The oxo complex is generated
              "in situ" by adding 3 equivalents of 0.2 M H₂O₂.

Figure 4-7  UV/Visible Spectrum in $H_2O$ of
a) [Ru(IV)O(dmp)$_2$S](PF$_6$)$_2$
b) [Ru(IV)O(dmp)$_2$S](PF$_6$)$_2$ After Exposure to 3 Atmospheres $O_2$.
c) cis-[Ru(VI)(O)$_2$(dmp)$_2$](PF$_6$)$_2$
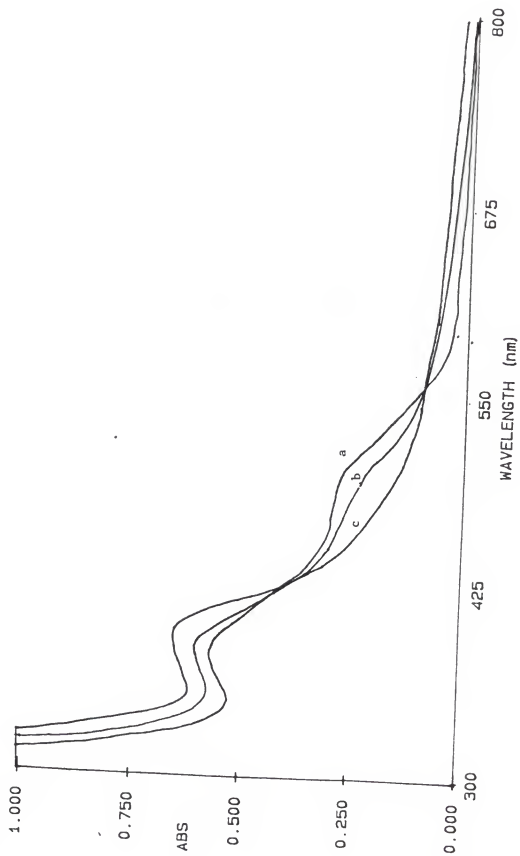
proposed mechanism in which the Ru(VI)(O)$_2$ species acts as an oxygen atom transfer agent. Oxidation reactions using cis-dioxo complexes of ruthenium, commonly results in the cleavage of carbon-carbon double bonds. Ruthenium tetroxide in combination with an oxygen source, is a powerful reagent for the cleavage of carbon-carbon double bonds to produce ketones and carboxylic acids.[29] Kaneda and co-workers have reported[111] that RuO$_2$, in the presence of acetaldehyde, catalyzes the oxidative cleavage of carbon-carbon double bonds of terminal and a,b-unsaturated carbonyl compounds using O$_2$. Double bonds of terminal alkenes, e.g. octene and dodecene were cleaved to give the corresponding carboxylic acids. Although there are no literature reports of cis-dioxo complexes cleaving norbornene, exclusive epoxide formation is probably a function of the substrate chosen.

If the active species in this epoxidation reaction proceeds via an oxygen atom transfer mechanism, the addition of a radical trap should not have an effect on the reaction. When benzoquinone, the radical trap, was added to the reaction, initially starting with the Ru(IV)O species, or when the trap was added to the reaction of the Ru(II) complex after the induction period, there was no change in the activity of the catalyst. These experiments further support the proposed mechanism. The epoxidation reaction proceeds in 2 parts. The first part of the reaction, the formation of the Ru(IV)O species via a metal-alkylperoxide, involves radicals. Once formed, the Ru(IV)O species reacts via an oxygen atom transfer mechanism as proposed in Figure 4-5. The eventual leveling off of products may be due to the slow formation of the Ru(II) species in the reaction.

The oxidation of other olefins by the Ru(II) precursor was also investigated. The oxidation of *trans*-b-methyl styrene was used as a probe molecule to further support the proposed mechanism. This substrate produces either cleavage products or the epoxide. This reaction proceeded with the same 12 hour induction period observed with norbornene. As illustrated in Figure 4-8, the initial product observed in this reaction was the *trans*-epoxide. As the reaction proceeds, benzaldehyde, produced from the cleavage of the carbon-carbon double bond becomes the major product. After 48 hours of reaction time a 6 : 1 ratio of benzaldehyde : epoxide results. If the benzaldehyde was being produced from the high valent *cis*-dioxo species, the addition of $H_2O_2$, to generate exclusively the dioxo species should result in only the cleavage products being observed. When the *cis*-dioxo complex was generated, and maintained with the addition of $H_2O_2$, only benzaldehyde was observed. Furthermore, when a limited amount of $H_2O_2$ was added to the initial Ru(II) complex, to generate only the Ru(IV)O species, only epoxide is observed. These experiments further support the proposed mechanism.

The oxidation of terminal olefins was also studied using this sterically hindered ruthenium complex. Terminal olefins are difficult to selectively oxidize and often lead to allylic oxidation products.[112] Under the standard reaction conditions used above, 1-hexene was oxidized primarily to the cleavage product, pentanal. This product was identified via GC/MS. This oxidation proceeded with an 8 : 1 ratio of cleavage : epoxide. To further support the proposed mechanism,
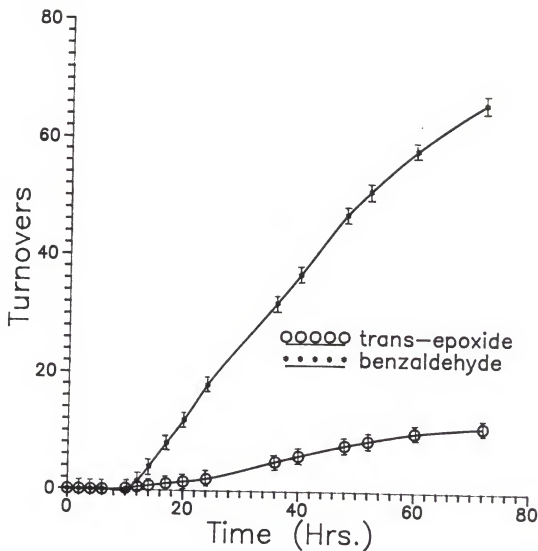
Figure 4-8    Oxidation of a 0.5 M CH₃CN Solution of *trans*-β-Methyl
              Styrene by 2 x 10⁻⁴ M (10⁻⁵ moles) of
              [Ru(dmp)₂(S)₂](PF₆)₂ at 65°C  and 3 Atmospheres.

analogous reactions were performed to that of styrene. When excess $H_2O_2$ was added to this reaction, generating the high valent $cis$-Ru(VI)(O)$_2$, only the cleavage product was observed. On the other hand, when a limited amount of $H_2O_2$ was added to the reaction mixture, to generate only the Ru(IV)(O) species, 1,2 epoxyhexane was observed exclusively. These experiments further support the proposed mechanism that the cleavage products are arise from the $cis$-Ru(VI)(O)$_2$ complex and that the epoxide comes from the Ru(IV)O species.

CHAPTER 5

THE OXIDATION OF ALKANES BY RUTHENIUM
DIMETHYL PHENANTHROLINE COMPLEXES

## Introduction

As previously mentioned, the activation of olefins has been
actively pursued by inorganic and organometallic chemists. These
studies are further evidence of the cooperativity and interdependence of
the fields of homogeneous catalysis and inorganic coordination
chemistry. The activation of alkanes has only recently received the
attention olefins have been receiving for decades. Since the end of the
1960s the activation of saturated hydrocarbons by transition metal
complexes has brought about new problems in the field of homogeneous
catalysis. In 1968, Jack Halpern[113] claimed that "the most important
and challenging problems in the whole field of homogeneous catalysis is
the development of a successful approach to the activation of C-H
bonds."

The inertness of alkanes is well known and is reflected in one of
their old names, "paraffins" (from the Latin parum affinis - without
affinity).[114,115] Known reactions of alkane require high temperatures or
reactive species, e.g., strong oxidants, superacids, radicals, and
carbenes. The understanding of the reactivity and mechanisms of these
reactions has industrial, as well biological implications.

111

## Background

As mentioned in Chapter 2, several industrial processes are based on the oxidation of saturated hydrocarbons using transition metals and $O_2$. These processes fall into the category of an autoxidation process as previously described. The utilization of transition metals in the oxidations of alkanes has been extensively studied using a variety of heterogeneous catalytic systems.[116] Methane is the most challenging substrate. The conversion of methane to methanol, a storable fuel, makes this oxidation reaction highly desirable.[117] Blair and Wheeler[118] first demonstrated that methane can be oxidized in the presence a catalyst. Since that first report, there have been a number of studies dealing with a variety of techniques and catalysts.

Catalysts based on $MoO_3$ have been the most widely studied heterogeneous systems for the partial oxidation of methane to methanol and formaldehyde. One of the most comprehensive early patents is that of ICI England.[119] High selectivities for methanol formation are found using a methane to oxygen ratio of 97 : 3, at 50 atmospheres and 430-500°C. These stringent reaction conditions are not uncommon for many heterogeneous metal-oxide based catalyst systems. In this work by ICI, the active catalyst was a mixed metal system of $Fe_2O_3 \cdot (MoO_3)_3$. This system proceeds with conversions of 2-3%.

More recently, Lunsford and co-workers[120] reported the partial oxidation of methane using a molybdenum on silica catalyst. In this work nitrous oxide was used as an oxidant. Once again, stringent conditions were employed (500°C). In this report, methane was oxidized to methanol and formaldehyde with a 78% selectivity and 3% conversion.

During the past decade, Atlantic Richfield Company has reported an extensive amount of work on the oxidation of methane to higher hydrocarbons.[121-127] In this work a manganese oxide based catalyst is capable of oxidizing methane to C2 or higher hydrocarbons with 80% selectivity and 25% conversion. Once again this system was carried out at extreme temperatures of 800-1200°C. This work by far has been the most encouraging to date for the formation of alternative fuels from the abundant feedstock of methane.

In the area of homogeneous oxidations of alkanes, much less work has been reported. Many of the reported homogeneous systems mimic a variety of enzymes, such as cytochrome P-450 and methane monooxygenase. In both of these enzymes the active center is believed to involve an iron-oxo center. Groves and co-workers[38] have reported that iron porphyrin system, Fe(TTP)Cl/iodosobenzene (TTP = 5,10,15,20-tetra-$o$-tolylporphyrin) is capable of aliphatic hydroxylations. In this work, cyclohexane is oxidized to a 15 : 1 ratio of cyclohexanol and cyclohexanone, respectively. It is proposed that this reaction proceeds via a radical mechanism with the first step of the reaction being a hydrogen atom abstraction. Kinetic isotope experiments resulted in a $k_H/k_D$ of 12.9. This $k_H/k_D$ value suggests substantial C-H bond breaking in the transition state of the reaction. Interestingly, as mentioned in Chapter 4, analogous iron porphyrin systems oxidize olefins via oxygen atom transfer, where, as illustrated here, the oxidation of alkane proceeds via a radical mechanism.[38,128] This has been observed for several other iron-oxo containing compounds.[129-131]

In the area of ruthenium-oxo chemistry, much less work has been reported for the oxidation of alkanes. Che and co-workers[132] report that the *trans*-ruthenium(VI) dioxo complex, *trans*-[Ru(VI)(O)$_2$(5,5'-Me$_2$bpy)$_2$](ClO$_4$)$_2$ (5,5' Me$_2$bpy = 5,5'-dimethyl-2,2'-bipyridine) is capable of oxidizing alkanes stoichiometrically. In this work cyclohexane is oxidized to cyclohexanone, and adamantane to 1-adamantanol. It is surprising that this complex has 100% selectivity to the 3° C-H bond in the adamantane reaction. To regenerate the active dioxo species an oxygen atom transfer reagent such as NaOCl was employed. Che has also reported[109] a similar chloride complex, *cis*-[Ru(VI)(O)$_2$(6,6'-Cl$_2$bpy)$_2$](ClO$_4$)$_2$ (6,6'-Cl$_2$bpy = 6,6'-dichloro-2,2'-bipyridine) is capable of stoichiometrically oxidizing cyclohexane to cyclohexanone.

In a recent report, Che and co-workers[134] reported that a series of ruthenium(II), *cis*-[Ru(II)(L)$_2$(OH$_2$)$_2$](CF$_3$SO3)$_2$ (L = substituted 2,2'-bipyridine or 1,10 phenanthroline) complexes are capable of catalytically oxidizing alkanes in the presence of t-butylhydroperoxide. In this study cyclohexane is oxidize primarily to cyclohexanol and cyclohexanone. Other linear alkanes, such as n-hexane and n-heptane are non-selectively oxidize to a variety of alcohol and ketone products. Out of the reported complexes used in this study, the dichloro bypyridine complex, *cis*-Ru(6,6'-Cl$_2$bpy)$_2$(OH$_2$)$_2^{2+}$ was shown to be the most active. In a typical reaction for the oxidation of cyclohexane, 420 turnovers/12 hours resulted. This reaction was shown to proceed via a radical mechanism with the first step being a hydrogen atom abstraction. In a kinetic isotope experiment, a $k_H/k_D$ of 3.5 resulted using d$^6$

cyclohexane. This $k_H/k_D$ value clearly indicates that this reaction involve the breaking of C-H bonds.

## Scope of Catalysis

Standard oxidation setups as described in Chapter 2 were used. The oxidations were comprised of 25-35 mL of solvent and 15-25 mL of substrate, 1 mL of benzene as an internal GC standard and $10^{-5}$ moles of catalyst. In these reactions $10^{-2}$ moles of $H_2O_2$ were used as an oxidant, since safety restraints prevented the use of $O_2$ with gaseous substrates. This amount of $H_2O_2$ would assure that there would be enough oxidant present for the reaction to go to completion. The standard was omitted when it interfered with the quantitative analysis of the products in some oxidations. The temperature was maintained at 75°C by an oil bath, and the initial pressure of 50 psig of air or substrate were used in all cases. Products were determined using GC and GC/MS as described in Chapter 2. Appropriate calibration curves were constructed and used to quantify the products. In these oxidation reactions blanks were performed using all components except the catalyst to assure oxidation was caused by the metal catalyst. Extreme caution should be used when working with these reactions. The safety precautions outlined in Chapter 2 should be followed here.

## Results and Discussion

As mentioned above, the oxidation of methane to methanol, a storable fuel, is a highly desirable objective.[117] For this reason and for the challenge of oxidizing this most difficult substrate, the

oxidation of methane was studied using the sterically hindered ruthenium (II) complex, cis-[Ru(II)(dmp)$_2$(S)$_2$](PF$_6$)$_2$ (S = H$_2$O or CH$_3$CN), and H$_2$O$_2$. Methane was oxidized[135] under the reaction conditions described above, to a 4 : 1 ratio of methanol and formaldehyde, as illustrated in Figure 5-1. The solvent can be either H$_2$O or CH$_3$CN using either the diaquo or the bis-acetonitrile analogue of the Ru(dmp) complex. In water, the reaction proceeds with a 1.5% conversion (120 turnovers/24 hours) and in acetonitrile with a 1.9% conversion(140 turnovers/24 hours). This reaction proceeds with a 4-hour induction period and after 24 hours a loss of activity is observed. Blank reactions without CH$_4$ did not yield oxidation products showing that methanol was not produced from ligand decomposition. Utilizing OCl$^-$ as an oxidant with cis-[Ru(dmp)$_2$(OH$_2$)](PF$_6$)$_2$, gave rise to similar results as the H$_2$O$_2$/H$_2$O system, although slightly lower conversion was observed (1.2%). In this system, trace amounts of chloroform and dichloromethane are observed. This reaction can also be carried out using Oxone (peroxysulfate) as the oxidant with conversions comparable to OCl$^-$.

As illustrated in Figure 5-2 several free radical experiments were performed to determine if radicals were involved in this oxidation reaction. The addition of AIBN (a free radical initiator, azo-bis(isobutyronitrile)) to the methane oxidation in acetonitrile resulted in only a slight increase in activity. In this reaction, greater than 1% of the products observed are dimethyl ether and coupling products (methylethylether, ethane, etc.). Addition of AIBN, without any catalyst present, resulted in no oxidation. In the presence of the free radical inhibitor, benzoquinone, no oxidation are observed. If
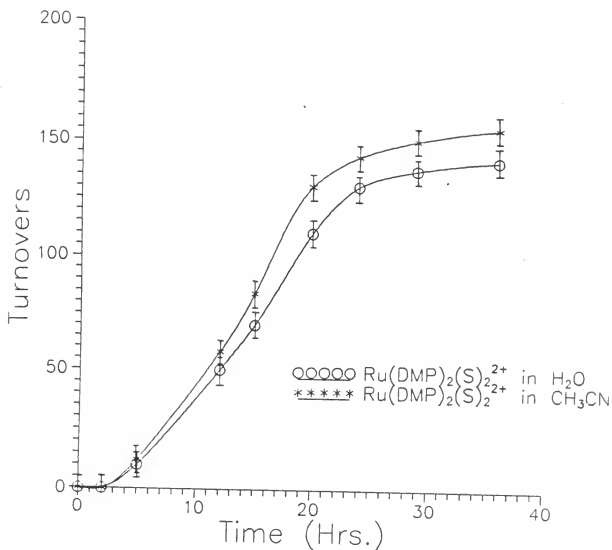
Figure 5-1    Oxidation of Methane (50 psig) by 2 x 10⁻⁴ M (10⁻⁵ moles) of [Ru(dmp)₂(S)₂](PF₆)₂ with H₂O₂ (10⁻² moles) at 75°C.
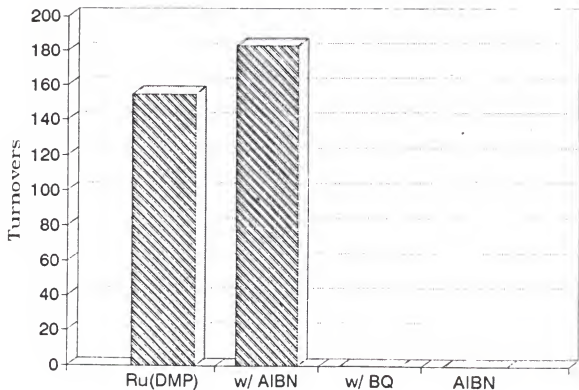
Figure 5-2    Free Radical Experiments for the Oxidation of Methane (50 psig) by $2 \times 10^{-4}$ M ($10^{-5}$ moles) of $[Ru(dmp)_2(S)_2](PF_6)_2$ with $H_2O_2$ ($10^{-2}$ moles) at 75°C.

benzoquinone is added to the reaction after the induction period, in a similar fashion described in Chapter 4, no oxidation products are observed. These experiments clearly suggest that radicals are involved in this oxidation.

A series of radical trapping experiments were carried out using bromotrichloromethane, as well as carbon tetrachloride. In these experiments a variety of halogenated products are observed ranging from chloroform to brominated products such as dibromomethane further supporting the involvement of a radical mechanism. These results are not surprising since as mentioned above, iron-oxo complexes epoxidize olefins via oxygen atom transfer reactions and hydroxylate alkanes via radical mechanisms. These same results seem to hold for ruthenium-oxo complexes. As demonstrated in Chapter 4, this sterically hindered ruthenium complex epoxidizes olefins via an oxygen atom transfer mechanism or cleaves carbon-carbon double bonds. As illustrate above this complex will oxidize alkanes via a radical mechanism.

To further elucidate the mechanism of this reaction, a series of experiments were performed to determine if the first step of this reaction was the abstraction of a hydrogen atom. This was accomplished by studying the oxidation of cyclohexane and comparing it to $d^6$ cyclohexane. Cyclohexane was used in these experiments because of the availability and cost of the deuterated analogue. If the rates of these experiments are compared, a $k_H/k_D$ could be obtained, determining whether C-H bond breakage is involved in the reaction mechanism. The results of these experiments are illustrated in Figure 5-3. With a large excess of substrate, the reactions are zero order in substrate. The rates
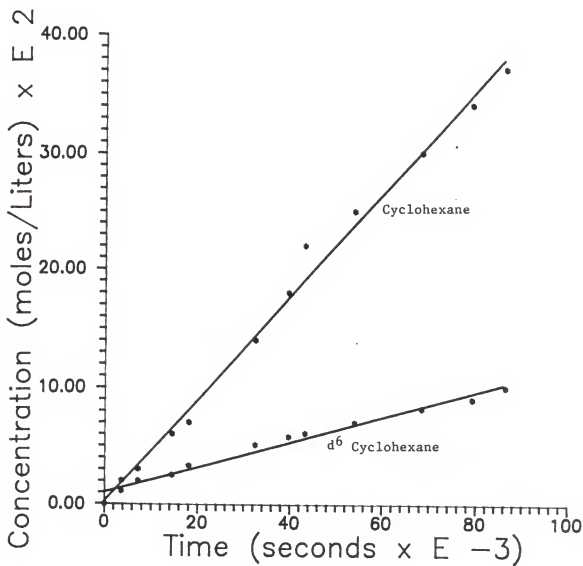
Figure 5-3    Deuterium Isotope Effect in the Oxidation of Cyclohexane at 75° using $2 \times 10^{-4}$ M ($10^{-5}$ moles) of $[Ru(dmp)_2(S)_2](PF_6)_2$ with $H_2O_2$ ($10^{-2}$ moles).

obtained from the plot of concentration of product vs. time are: $k_H$ = 4.36 x $10^{-6}$ moles.$L^{-1}$.$sec^{-1}$ and $k_D$ = 1.07 x $10^{-6}$ moles.$L^{-1}$.$sec^{-1}$. These rates result in a kinetic isotope effect of 4.0. This $k_H/k_D$ is similar to that reported by Che[134] ($k_H/k_D$ = 3.5) for the oxidation of cyclohexane by a $cis$-Ru(O)$_2$ complex using t-butylhydroperoxide as the oxidant. Based on these results, the oxidation of alkanes by the sterically hindered $cis$-[Ru(dmp)$_2$(S)$_2$](PF$_6$)$_2$ proceeds via a radical mechanism, with the first step of the reaction involving the breaking of a C-H bond.

The proposed mechanism for the oxidation of alkanes by this sterically hindered ruthenium complex is illustrated in Figure 5-4. In this reaction the first step of the mechanism is the abstraction of a hydrogen atom from the alkane to produce an alkyl radical and a ruthenium-hydroxide species. The active metal center, the Ru=O moiety can be thought of as a Ru-O$^-$ species, which would function as a radical capable of abstracting a hydrogen atom from the alkane. There are many reports of iron-oxo centers functioning as hydrogen atom abstractors.[38,136-138] Furthermore, the hydrogen isotope value obtained for this ruthenium complex is indicative of a free radical abstraction mechanism.[139] In the next step of the mechanism, the hydroxy ligand on the ruthenium is then transferred to the resulting radical to produced the alcohol product. This is essentially the same mechanism that has been proposed for the oxidation of alkanes by cytochrome P-450.[140,141] Similar mechanisms have been proposed using iron porphyrin systems,[36,142] as well as several ruthenium complexes.[109,143,144] This type of mechanism has been labeled a rebound mechanism.[88] The high valent active
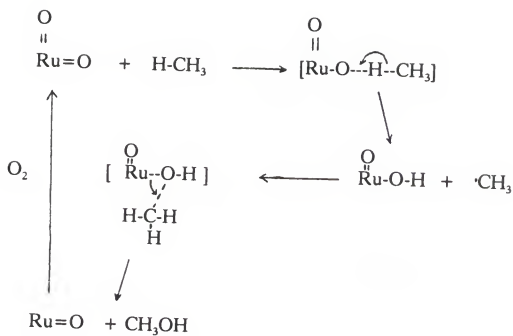
Figure 5-4    Proposed Mechanism for the Oxidation of
Methane by [Ru(dmp)$_2$(S)$_2$](PF$_6$)$_2$ with H$_2$O$_2$.

ruthenium-oxo species was regenerated by the addition of $O_2$, as described in Chapter 4.

Several other alkanes have been oxidized using this ruthenium complex. Ethane was oxidized in a similarly fashion to methane to a 4 : 1 ratio of ethanol and acetaldehyde. This reaction proceeds with a 2.3 % conversion in 24 hours, slightly higher then the methane reaction. Propane was also shown to be selectively oxidized to a 5 : 2 : 1 ratio of 1-propanol, 1-propanal and 2-propanol, respectively. Trace amounts of acetone were also observed in this reaction. This reaction proceeded with a 3 % conversion. Adamantane was also found to be oxidized to 1-adamantanol. After 18 hours of reaction time, 2-adamantanol and 2-adamantanone were observed. The amount of products produced in the oxidation of adamantane were not quantified. These results for the oxidation of adamantane are analogous to those found by Che.[132] Che found that the oxidation of adamantane by the trans-ruthenium dioxo complex, trans-[Ru(VI)(O)$_2$(5,5′-Me$_2$bpy)$_2$](ClO$_4$)$_2$, resulted in exclusively 1-adamantanol in 12 hours. Based on these experiments it seems our ruthenium complex preferentially attacks 1° or 3° C-H bonds, before 2° C-H bonds. Steric restraints may contribute partly to this pattern of reactivity.

The nature of the catalyst during the reaction was investigated. As mentioned above, the activity of the catalyst ceased after 24 hours of reaction time. Upon recovering the catalyst after the reaction has ceased, the $^1$H NMR shows dramatic changes from the starting compound. This is illustrated in Figure 5-5 where the phenanthroline region of the

Figure 5-5     $^1$H NMR of the Phenanthroline Region of $[Ru(dmp)_4(OH_2)_2](PF_6)_2$ Before and After the Oxidation of Methane at 75°C and 50 psig.

Before Catalysis
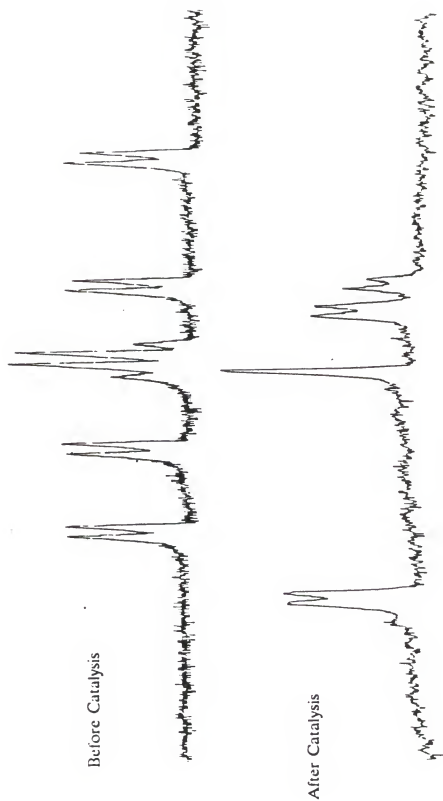
After Catalysis

catalyst before and after catalysis are compared. A dramatic change has occurred in this region during the reaction. Comparing the catalyst to the free dmp ligand does not explain the observed resonances and indicates that dissociation of the ligand is not occurring. One explanation of this change in the ligand resonance is that the catalyst is oxidizing the ligand system. In this ligand the methyl groups are most susceptible to oxidation. If they are oxidized to carboxylate groups, dimers, polymers or aggregates could form. The $^{13}$C NMR did not show any carbonyl groups in the oxidized catalyst. The oxidation of ligand systems by active catalysts is not an uncommon problem and has been observed for both Schiff base complexes[145] and a variety of different porphyrin systems.[146] To overcome this problem, the halogenation of the methyl groups, or the entire phenathroline ligand could be attempted. Traylor and co-workers[147,148] have reported that upon fluorinating a porphyrin system, an increase in activity and catalyst lifetime was observed. Fluorinating the methyl groups may also increase the activity of our catalyst, as well as increase its lifetime.

Different ligand systems have a dramatic influence on the activity of transition metal catalyst for the oxidation of organic substrates. The complexes studied here catalyze both autoxidation reactions and the selective oxidation of olefins and alkanes. The use of molecular oxygen as the primary oxidant, in combination with these complexes, has made these studies unique.

The use of the cobalt-acetonitrile complex, $[Co(NCCH_3)_4](PF_6)_2$ for the oxidation of alkanes, via an autoxidation mechanism, showed several unique properties. The ability to oxidize alkanes under mild reaction conditions (75°C and 3 atmospheres) makes this reaction desirable from an industrial standpoint. Furthermore, this complex demonstrated the ability of an oxidized cobalt complex to initiate the reaction, in the absence of an external radical initiator which is commonly employed industrially. In addition to initiation, this cobalt catalyst efficiently catalyzes the decomposition of peroxides to the observed products. Unfortunately, water, a by-product from the reaction, inhibits the activity of this complex. This warrants the investigation of cobalt complexes with similar ligand systems, which are resistant to the water formed during the oxidation.

The sterically hindered ruthenium complex, $[Ru(dmp)_2(S)_2](PF_6)_2$, as an oxidation catalyst, demonstrates remarkable activity towards the

oxidation of a variety of organic substrates. The aerobic oxidation of olefins proceeds through a unique mechanism involving the formation of an alkylperoxide. This peroxide is the source of the active high valent ruthenium-oxo catalyst. The ability to selectively control the product distribution using $H_2O_2$ as an oxidant demonstrates the versatility of this complex for the oxidation of olefins.

This sterically hindered ruthenium complex has also been shown to be an active catalyst for the selective oxidation of alkanes. The ability to oxidize methane under mild reaction conditions shows promise for the conversion of this abundant feedstock to a storable fuel. This reaction has been shown to proceed via a radical mechanism with the first step of the reaction being the abstraction of a hydrogen atom. By modifying the phenanthroline ligand system, a more resistant complex can be synthesized. Based on literature precedence, chloro or fluoro groups should increase the activity of this system, as well as increase the catalyst lifetime.

The mechanisms by which this sterically hindered ruthenium complex proceeds are analogous to those reported for iron systems. The oxidation of olefins proceeds via an oxygen atom transfer mechanism and the oxidation of alkanes proceed via a radical mechanism. This further demonstrates the practicality of using ruthenium complexes to help in the understanding of various iron based enzymes found in living organisms.

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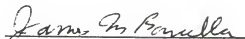
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